

Under the Paperwork Reduction Act of 1995 no persons are required to respond to a collection of information unless it displays a valid OMB control number

Effective on 12/08/2004.

Pursuant to the Consolidated Appropriations Act, 2005 (H.R. 4818).

**FEE TRANSMITTAL**  
**For FY 2009**☐ Applicant claims small entity status. See 37 CFR 1.27**TOTAL AMOUNT OF PAYMENT** (\$) 540.00**Complete if Known**

Application Number	10/801,424
Filing Date	March 16, 2004
First Named Inventor	HU, Ruizhong, et al.
Examiner Name	BRUNSMAN, David M.
Art Unit	1793
Attorney Docket No.	W9570-01

**METHOD OF PAYMENT (check all that apply)**☐ Check ☐ Credit Card ☐ Money Order ☐ None ☐ Other (please identify): \_\_\_\_\_☒ Deposit Account Deposit Account Number: 07-1770 Deposit Account Name: W. R. Grace & Co. - Conn.

For the above-identified deposit account, the Director is hereby authorized to: (check all that apply)

☒ Charge fee(s) indicated below ☐ Charge fee(s) indicated below, except for the filing fee☐ Charge any additional fee(s) or underpayments of fee(s) under 37 CFR 1.16 and 1.17 ☐ Credit any overpayments**WARNING:** Information on this form may become public. Credit card information should not be included on this form. Provide credit card information and authorization on PTO-2038.**FEE CALCULATION****1. BASIC FILING, SEARCH, AND EXAMINATION FEES**

Application Type	FILING FEES		SEARCH FEES		EXAMINATION FEES		Fees Paid (\$)
	Fee (\$)	Small Entity Fee (\$)	Fee (\$)	Small Entity Fee (\$)	Fee (\$)	Small Entity Fee (\$)	
Utility	330	165	540	270	220	110	
Design	220	110	100	50	140	70	
Plant	220	110	330	165	170	85	
Reissue	330	165	540	270	650	325	
Provisional	220	110	0	0	0	0	

**2. EXCESS CLAIM FEES****Fee Description**

	Fee (\$)	Small Entity Fee (\$)
Each claim over 20 (including Reissues)	52	26
Each independent claim over 3 (including Reissues)	220	110
Multiple dependent claims	390	195

<b>Total Claims</b>	<b>Extra Claims</b>	<b>Fee (\$)</b>	<b>Fee Paid (\$)</b>	<b>Multiple Dependent Claims</b>
- 20 or HP = _____ x _____ = _____				<b>Fee (\$)</b> <b>Fee Paid (\$)</b>

HP = highest number of total claims paid for, if greater than 20.

<b>Indep. Claims</b>	<b>Extra Claims</b>	<b>Fee (\$)</b>	<b>Fee Paid (\$)</b>
- 3 or HP = _____ x _____ = _____			

HP = highest number of independent claims paid for, if greater than 3.

**3. APPLICATION SIZE FEE**

If the specification and drawings exceed 100 sheets of paper (excluding electronically filed sequence or computer listings under 37 CFR 1.52(e)), the application size fee due is \$270 (\$135 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).

<b>Total Sheets</b>	<b>Extra Sheets</b>	<b>Number of each additional 50 or fraction thereof</b>	<b>Fee (\$)</b>	<b>Fee Paid (\$)</b>
- 100 = _____ / 50 = _____ (round up to a whole number) x _____ = _____				

**4. OTHER FEE(S)**

Non-English Specification, \$130 fee (no small entity discount)

Other (e.g., late filing surcharge): Appeal Brief Fee

**Fees Paid (\$)**

\$540.00

**SUBMITTED BY**

Signature	Registration No. 32,406 (Attorney/Agent)	Telephone 410-531-4518
Name (Print/Type) Charles A. Cross		Date March 17, 2009

This collection of information is required by 37 CFR 1.136. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 30 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.



Under the Paperwork Reduction Act of 1995 no persons are required to respond to a collection of information unless it displays a valid OMB control number

Effective on 12/08/2004.

Fees pursuant to the Consolidated Appropriations Act, 2005 (H.R. 4818).

# FEE TRANSMITTAL

## For FY 2009

☐ Applicant claims small entity status. See 37 CFR 1.27

TOTAL AMOUNT OF PAYMENT (\$) 540.00

### Complete if Known

Application Number	10/801,424
Filing Date	March 16, 2004
First Named Inventor	HU, Ruizhong, et al.
Examiner Name	BRUNSMAN, David M.
Art Unit	1793
Attorney Docket No.	W9570-01

### METHOD OF PAYMENT (check all that apply)

☐ Check ☐ Credit Card ☐ Money Order ☐ None ☐ Other (please identify): \_\_\_\_\_

☒ Deposit Account Deposit Account Number: 07-1770 Deposit Account Name: W. R. Grace & Co. - Conn.

For the above-identified deposit account, the Director is hereby authorized to: (check all that apply)

☒ Charge fee(s) indicated below ☐ Charge fee(s) indicated below, except for the filing fee

☐ Charge any additional fee(s) or underpayments of fee(s) under 37 CFR 1.16 and 1.17 ☐ Credit any overpayments

WARNING: Information on this form may become public. Credit card information should not be included on this form. Provide credit card information and authorization on PTO-2038.

### FEE CALCULATION

#### 1. BASIC FILING, SEARCH, AND EXAMINATION FEES

Application Type	FILING FEES		SEARCH FEES		EXAMINATION FEES		Fees Paid (\$)
	Fee (\$)	Small Entity Fee (\$)	Fee (\$)	Small Entity Fee (\$)	Fee (\$)	Small Entity Fee (\$)	
Utility	330	165	540	270	220	110	
Design	220	110	100	50	140	70	
Plant	220	110	330	165	170	85	
Reissue	330	165	540	270	650	325	
Provisional	220	110	0	0	0	0	

#### 2. EXCESS CLAIM FEES

##### Fee Description

	Fee (\$)	Small Entity Fee (\$)
Each claim over 20 (including Reissues)	52	26
Each independent claim over 3 (including Reissues)	220	110
Multiple dependent claims	390	195

<b>Total Claims</b>	<b>Extra Claims</b>	<b>Fee (\$)</b>	<b>Fee Paid (\$)</b>	<b>Multiple Dependent Claims</b>	<b>Fee (\$)</b>	<b>Fee Paid (\$)</b>
- 20 or HP =	x	=				

HP = highest number of total claims paid for, if greater than 20.

<b>Indep. Claims</b>	<b>Extra Claims</b>	<b>Fee (\$)</b>	<b>Fee Paid (\$)</b>
- 3 or HP =	x	=	

HP = highest number of independent claims paid for, if greater than 3.

#### 3. APPLICATION SIZE FEE

If the specification and drawings exceed 100 sheets of paper (excluding electronically filed sequence or computer listings under 37 CFR 1.52(e)), the application size fee due is \$270 (\$135 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).

<b>Total Sheets</b>	<b>Extra Sheets</b>	<b>Number of each additional 50 or fraction thereof</b>	<b>Fee (\$)</b>	<b>Fee Paid (\$)</b>
- 100 =	/ 50 =	(round up to a whole number) x	=	

#### 4. OTHER FEE(S)

Non-English Specification, \$130 fee (no small entity discount)

Other (e.g., late filing surcharge): Appeal Brief Fee

**Fees Paid (\$)**

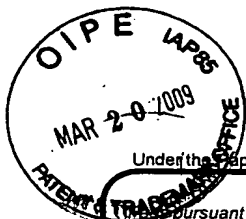
\$540.00

### SUBMITTED BY

Signature	Registration No. 32,406 (Attorney/Agent)	Telephone 410-531-4518
Name (Print/Type) Charles A. Cross	Date March 17, 2009	

This collection of information is required by 37 CFR 1.136. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 30 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.



PTO/SB/17 (10-08)

Approved for use through 06/30/2010. OMB 0651-0032

U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

Under the Paperwork Reduction Act of 1995 no persons are required to respond to a collection of information unless it displays a valid OMB control number

Effective on 12/08/2004.

Pursuant to the Consolidated Appropriations Act, 2005 (H.R. 4818).

**FEE TRANSMITTAL**  
**For FY 2009**☐ Applicant claims small entity status. See 37 CFR 1.27

TOTAL AMOUNT OF PAYMENT (\$) 540.00

**Complete if Known**

Application Number	10/801,424
Filing Date	March 16, 2004
First Named Inventor	HU, Ruizhong, et al.
Examiner Name	BRUNSMAN, David M.
Art Unit	1793
Attorney Docket No.	W9570-01

**METHOD OF PAYMENT** (check all that apply)☐ Check ☐ Credit Card ☐ Money Order ☐ None ☐ Other (please identify): \_\_\_\_\_☒ Deposit Account Deposit Account Number: 07-1770 Deposit Account Name: W. R. Grace & Co. - Conn.

For the above-identified deposit account, the Director is hereby authorized to: (check all that apply)

☒ Charge fee(s) indicated below ☐ Charge fee(s) indicated below, except for the filing fee☐ Charge any additional fee(s) or underpayments of fee(s) under 37 CFR 1.16 and 1.17 ☐ Credit any overpayments**WARNING:** Information on this form may become public. Credit card information should not be included on this form. Provide credit card information and authorization on PTO-2038.**FEE CALCULATION****1. BASIC FILING, SEARCH, AND EXAMINATION FEES**

Application Type	FILING FEES		SEARCH FEES		EXAMINATION FEES		Fees Paid (\$)
	Fee (\$)	Small Entity Fee (\$)	Fee (\$)	Small Entity Fee (\$)	Fee (\$)	Small Entity Fee (\$)	
Utility	330	165	540	270	220	110	
Design	220	110	100	50	140	70	
Plant	220	110	330	165	170	85	
Reissue	330	165	540	270	650	325	
Provisional	220	110	0	0	0	0	

**2. EXCESS CLAIM FEES****Fee Description**

Each claim over 20 (including Reissues)

**Fee (\$)****Small Entity Fee (\$)**

52 26

Each independent claim over 3 (including Reissues)

220 110

Multiple dependent claims

390 195

**Total Claims** **Extra Claims** **Fee (\$)** **Fee Paid (\$)****Multiple Dependent Claims**

- 20 or HP = \_\_\_\_\_ x \_\_\_\_\_ = \_\_\_\_\_

**Fee (\$)** **Fee Paid (\$)**

HP = highest number of total claims paid for, if greater than 20.

**Indep. Claims** **Extra Claims** **Fee (\$)** **Fee Paid (\$)**

- 3 or HP = \_\_\_\_\_ x \_\_\_\_\_ = \_\_\_\_\_

HP = highest number of independent claims paid for, if greater than 3.

**3. APPLICATION SIZE FEE**

If the specification and drawings exceed 100 sheets of paper (excluding electronically filed sequence or computer listings under 37 CFR 1.52(e)), the application size fee due is \$270 (\$135 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).

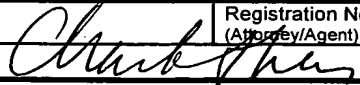
**Total Sheets** **Extra Sheets** **Number of each additional 50 or fraction thereof** **Fee (\$)** **Fee Paid (\$)**

- 100 = \_\_\_\_\_ / 50 = \_\_\_\_\_ (round up to a whole number) x \_\_\_\_\_ = \_\_\_\_\_

**4. OTHER FEE(S)**

Non-English Specification, \$130 fee (no small entity discount)

**Fees Paid (\$)**Other (e.g., late filing surcharge): Appeal Brief Fee\$540.00**SUBMITTED BY**

Signature		Registration No. (Attorney/Agent) 32,406	Telephone 410-531-4518
Name (Print/Type)	Charles A. Cross		Date March 17, 2009

This collection of information is required by 37 CFR 1.136. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 30 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

PATENT



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE  
BEFORE THE BOARD OF PATENT APPEALS  
AND INTERFERENCES

In re application of : March 17, 2009  
HU, Ruizhong et al. : Group Art Unit: 1793  
Serial No. 10/801,424 : Examiner: BRUNSMAN, David M  
Filed: March 16, 2004 : Docket No.: W9570-01  
For: Gasoline Sulfur Reduction Catalyst For Fluid Catalytic Cracking  
Process

**APPEAL BRIEF**

Mail Stop Appeal Brief-Patent  
Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

Sir/Madam:

This Appeal Brief is filed pursuant to Appellants' Notice of Appeal mailed on December 17, 2008. Appellants have enclosed a Request for Extension of Time for extending the deadline by one month for submitting the Brief, the payment of the applicable fees having been authorized in the Request.

## **Table of Contents**

<b>Statement of Real Party in Interest</b> .....	3
<b>Statement of Related Cases</b> .....	3
<b>Jurisdictional Statement</b> .....	3
<b>Table of Authorities</b> .....	4
<b>Status of Amendments</b> .....	5
<b>Grounds of Rejections to be Reviewed</b> .....	5
<b>Statement of Facts</b> .....	6
<b>Argument</b> .....	10
<b>Conclusion</b> .....	22
<b>Appendix</b> .....	23
1. <i>Claims Section</i> .....	23
2. <i>Claim Support</i> .....	37
3. <i>Evidence Section</i> .....	38

### **Statement of Real Party in Interest**

The real party of interest in the above-identified patent application is W.R. Grace & Co.-Conn.

### **Statement of Related Cases**

The Appellants are not aware of related prior or pending appeals, interferences, or judicial proceedings.

### **Jurisdictional Statement**

The Board has jurisdiction of this Appeal under 35 USC 134(a). The Examiner mailed a final rejection on August 18, 2008, setting a three-month shortened statutory period for response. The time for responding to the final rejection expired on November 18, 2008. A notice of appeal and request for a one-month extension of time under Rule 136 was filed on December 17, 2008. The two month period of time for filing the Appeal Brief is being extended under Rule 136 by one month to March 17, 2009.

## **Table of Authorities**

35 USC §103(a).....	5,12,15,18,20
35 USC 102 .....	18
Bausch & Lomb, Inc. v. Barnes-Hind/Hydrocurve, Inc., 230 U.S.P.Q. 416 (Fed. Cir. 1986).....	15
<i>In re Dow Chem. Co.</i> , 5 U.S.P.Q. 2d 1529 (Fed. Cir. 1988) .....	16
<i>In re Shetty</i> , 195 USPQ 753 (C.C.P.A. 1977).....	18
<i>In re Wesslau</i> , 147 U.S.P.Q. 391 (C.C.P.A. 1965) .....	21

### **Status of Amendments**

An amendment filed by Applicants on November 18, 2008 was entered by the Examiner pursuant to an Advisory Action mailed on November 26, 2008.

### **Grounds of Rejections to be Reviewed**

The August 18, 2008 final rejection contains three rejections. The rejection of claims 1-29 and 31-44 as being unpatentable under 35 USC §103(a) over US Patent 5,686,374 (Nakaoka) in view of US 4,627,911 (Chen) is the only one of the three rejections being reviewed herein. The amendment to claim 1 entered by the Examiner included subject matter of claim 43, and all of the remaining claims are dependent on claim 1. Since all of the rejected claims are dependent on claim 1 and the above rejection is the only rejection of the three relating to claim 43, the other two remaining rejections in the August 18, 2008 final rejection do not apply. It is therefore further submitted that failure to address those rejections herein should in no way be deemed an acquiescence or concurrence with those rejections.



### **Statement of Facts**

1. Claim 1, as amended, recites a cracking catalyst composition capable of being maintained in a fluidized state within a fluid cracking catalyst unit.
2. Claim 1 recites that the composition comprises zeolite, Lewis-Acid component, inorganic oxide matrix, and 0.20 percent by weight or less  $\text{Na}_2\text{O}$ .
3. Claim 1 was amended after August 18, 2008 final rejection to further recite that the average particle size of the catalyst is in the range of 20 to 150 microns.
4. Nakaoka relates to hydroprocessing catalyst compositions having diameters of 1.6 millimeters (1600 microns). *See* Col. 1, line 1; and Example 1, column 5, line 63.
5. Nakaoka discloses hydroprocessing catalyst compositions comprising zeolite, Group VI or Group VIII metals having hydrogenation properties, e.g., zinc, nickel and/or other metals. *See* Col. 2, line 5 and line 14.
6. Examiner relies on Nakaoka disclosure on Col. 2, line 57, that the zeolite in Nakaoka's catalyst contains less than 0.5 weight %  $\text{Na}_2\text{O}$ . *See* page 2 of August 18, 2008 Office Action.

7. Examiner admits on page 3 of the August 18, 2008 final rejection that Nakaoko is silent as to the sodium content of the catalyst composition as a whole, e.g., including matrix, and the hydrogenation metal.
8. Examiner relies on the allegation in 7. above and Example 4 and Example 6 for rejecting claims 2-7, 29, and 33-36 with respect to the amounts of  $\text{Na}_2\text{O}$  recited therein, which relate to the sodium content of the catalyst as a whole, which as indicated above, is 0.20  $\text{Na}_2\text{O}$  % by weight or less.
9. Examiner relies on Nakaoka's disclosure, e.g. , on col. 3, line 56, for the proposition that Nakaoka's catalyst has a Lewis acid component, wherein the disclosure therein mentions zinc oxide.
10. Examiner admits Nakaoka does not expressly describe a composition as having "Lewis acidity". *See* Examiner's admission on page 3 of August 18, 2008 final rejection.
11. The Examiner relies on column 1, lines 27-33, of Chen as basis for maintaining the rejection of the aforementioned claims. *See* page 4 of August 18, 2008 final rejection.
12. The aforementioned text in Chen states zeolite catalysts are known to be in the range of 1-140 microns.

13. The same aforementioned section of Chen also mentions that fixed bed catalysts containing catalysts are well known and are no smaller than 1/25<sup>th</sup> inch (about 1000 microns or 1 millimeter).

14. The primary disclosure of Chen relates to a process for cracking hydrocarbons using zeolite and methanol, wherein the goal of Chen's invention is to protect the zeolite from adsorption of contaminants in the cracking reaction. *See* Abstract.

15. Chen describes a cracking process in which the zeolite exits the reaction as waste, and therefore is not regenerated or recirculated to the cracking reactor. *See* Abstract, Column 5, lines 12-16, and Figure 1 where catalyst exits from unit at line identified as 55.

16. Chen describes using finely divided zeolite crystals having a mean particle size of  $3 \times 10^{-4}$  cm (3 microns). *See* column 4, line 38, and col. 3, line 53.

17. Examiner alleges that Chen exemplifies a particular case of the general teaching of "Fluidized Engineering" (Appendix A, also referred to herein as "Geldart"), i.e., the Examiner alleges this shows that the efficiency of a fluidized bed operation is maximized when the particles fall within the Geldart classification. *See* page 4 of August 18, 2008 final rejection.

18. Geldart also discloses that particles greater than 1000 microns (class D), and by extension particles of 1.6 mm (1600 microns), are difficult to fluidize. *See* page 79 of Geldart, Appendix A.

19. Geldart also discloses that an enormous amount of gas would be needed to fluidize class D particles, and those amounts of gas would be more than required for chemical operations.

20. In maintaining the above rejection of claims 1-29 and 31-44, the Examiner also relies on Applicants' claims 16 and 17 as evidence that Applicants' invention is obvious. *See* Examiner's comments on page 2 of November 26, 2008 Advisory Action.

## **Argument**

Appellants' invention relates to a catalyst suitable for fluidized catalytic cracking (FCC). The catalyst has shown to reduce sulfur in gasoline fractions produced from the FCC unit. Reducing sulfur in gasoline fractions from FCC processes is increasingly important as governmental authorities and industry seek to reduce environmental pollution from automobile exhaust.

A fluidizable catalytic cracking, FCC, process always requires catalyst to be fluidizable to effectively perform in a FCC unit. Such catalysts typically have an average particle size in the range of 20 to 150 microns. A FCC catalyst comes in contact with liquid hydrocarbons under fluidized conditions at reactor temperatures, e.g., in the range of 400 to 700°C, and then transferred to a regenerator where residual carbon (coke) is removed from the catalyst particles at relatively high temperatures. The regenerated catalyst particulate is then reused in subsequent reactor cycles. The particle sizes recited above therefore facilitate the use of the catalyst in this manner, and are therefore significantly distinguishable from, e.g., a larger catalyst used in a fixed bed petroleum refining processes, such as hydroprocessing disclosed by Nakaoka, or much

smaller catalyst crystals such as the zeolite crystals using in the cracking process disclosed by Chen.

As stated above, the particulate catalyst of Appellants' invention, as recited in the rejected claims, comprises zeolite, matrix, and Lewis Acid component. The zeolite is active in producing gasoline fractions in a FCC unit. The matrix in the invention serves to support the zeolite in a material having a size sufficiently large enough to reduce the loss of catalyst through the regenerator's exhaust stack, while also providing a hardness to the particle to reduce loss of catalyst and particle size due to attrition. The Lewis acid component contributes to the gasoline reduction feature possessed by the invention. *See* Paragraph [019] of Appellants' specification. Appellants have discovered and shown that sodium content (e.g., levels commonly found in FCC catalysts) can affect the performance of the catalyst in terms of reducing sulfur, and it has been unexpectedly discovered that if the sodium level in a catalyst (measured as Na<sub>2</sub>O) is 0.20 weight percent or less, the catalyst's ability to reduce sulfur is significantly enhanced. *See* Appellants' Example 1.

Appellants submit that the Examiner has erred in relying on Nakaoka and Chen to reject claims 1-29 and 31- 44 under 35 USC 103(a).

Nakaoka

Nakaoka discloses compositions formulated and shaped as catalysts for use as hydroprocessing catalysts, not FCC catalysts. Hydroprocessing is designed to process heavy oils in the presence of hydrogen, while also removing contaminants such as metals, sulfur and nitrogen. While the zeolite Y is present in these compositions to crack the hydrocarbon feed, the metals discussed later below effect hydrogenation reactions in the presence of added hydrogen to cause removal of contaminant species in the feed. *See* Nakaoka Col. 4, line 63-Col. 5, line 19; and Example 1 where catalysts are evaluated for *hydrodesulfurization* and *hydrodenitrification*. The Nakaoka matrix is formulated to provide a millimeter size catalyst that is typical of the size used in fixed bed processes.

As mentioned in Appellants' December 17, 2008 amendment after final rejection, Nakaoka's hydroprocessing catalysts have diameters on the scale of 1.6 millimeters, which, it is submitted, is reflective of fixed bed

catalysts. *See* Example 1, column 5, line 63. *See* also Chen at col. 1, lines 27-33, wherein catalyst of such size are suitable for fixed bed applications. *See* also US 4,705,621, col. 4, lines 41-49, Appendix B. It is submitted that the size of Nakaoko's catalysts are clearly distinguishable from those of Appellants' invention. Indeed, such catalysts are larger in size and generally considered by those skilled in the art to not be fluidizable under normal chemical operations. *See* Geldart, Appendix A.

Indeed, it is respectfully submitted that Examiner's position that Nakaoka's catalyst is fluidizable as recited in claim 1 is untenable. The very reference relied upon (Geldart Appendix A) by the Examiner in supporting the proposition that Nakaoka's catalysts are fluidizable expressly states it would take enormous gas beyond that normally required by a chemical operation to fluidize particles greater than 1000 microns. *See* Figure 9 on page 78, and page 79 of Geldart in Appendix B.

The Examiner is also relying on Nakaoka's disclosure of zinc oxide for the proposition that Nakaoka's catalyst comprises a Lewis acid



component, since Appellants include zinc as a suitable Lewis acid component for their invention. Without admitting the zinc oxide in Nakaoka's catalyst would inherently possess Lewis acidity, or that one of ordinary skill would recognize it as having Lewis acidity, it is submitted that any inherent Lewis acidity present in Nakaoka's catalyst is at best appreciated by those skilled in the art as being present in the context of the catalysts disclosed by Nakaoka, i.e., hydoprocessing catalysts having a size on the scale of 1.6 mm. It is also submitted that those of the ordinary skill would recognize that the zinc and other metals are included for purposes of functioning as a hydrogenation catalyst in a hydroprocessing catalyst. Since Nakaoka is otherwise silent as to Lewis acidity, Appellants fail to see how one of ordinary skill would view Nakaoka and any inherent Lewis acidity beyond that context. To do so, Appellants respectfully submit would amount to hindsight reconstruction of Nakaoka's teaching by utilizing Appellants' invention. Appellants submit the Examiner has recognized an undisclosed property only after reviewing Appellants invention, and then improperly applying that undisclosed property as a "teaching" applicable to an invention of a different composition not disclosed by Nakaoka, i.e., one that is fluidizable having an average particle size in the range recited in claim 1.

It is black letter law that hindsight reconstruction of the invention is impermissible under 35 USC 103(a). *See Bausch & Lomb, Inc. v. Barnes-Hind/Hydrocurve, Inc.*, 796 F. 2d 443, 230 U.S.P.Q. 416, 419 (Fed. Cir. 1986).

As submitted above and earlier in Appellants's December 17, 2008 response, the metals in Nakaoka's zeolite-containing catalysts are hydrogenating metals, such as nickel. It is submitted that such metals are specifically selected to catalyze hydrogenation that brings about removal of contaminant species in the presence of hydrogen to treat feedstock. Such metals, however, are not particularly desired for FCC catalysts. For example, FCC processes do not typically utilize hydrogen. It is submitted that there would be no need identified by Nakaoka to include a hydrogenation metal in FCC catalyst, and therefore it is submitted that there is no suggestion to include the metal in a particulate formed to be used as a catalyst in FCC processes.

As referenced earlier in Appellants' December 18, 2008 amendment after final rejection, certain hydrogenation catalyst metals are also considered poisonous to a FCC catalyst. *See* page 342 of "Fluid Catalytic Cracking:

Science and Technology (1993), Appendix C. It is therefore submitted that those of ordinary skill in the art would avoid Nakaoka's teachings when considering a composition for FCC catalysts, and that Appendix C teaches away from Appellants' invention.

It is further noted that the Examiner noted in the November 26, 2008 Advisory Action that the recitation of the metals disclosed by Nakaoka in claims 16 and 17 disproves or somehow undercuts Appellants' arguments that certain of Nakaoka's metals are poisonous for FCC catalysts. Appellants respectfully submit such a basis or rationale for maintaining the aforementioned obviousness rejection amounts to utilizing Appellants' own disclosure as motivation to utilize such metals. Such reliance on Appellants' disclosure is impermissible, and any motivation to utilize the Lewis acidity component must arise from the prior art. *See In re Dow Chem. Co.*, 5 U.S.P.Q. 2d 1529, 1531-1532 (Fed. Cir. 1988).

The Examiner relies upon column 2, line 57 in Nakaoka for the proposition that it is known to utilize FCC catalyst compositions having a sodium content of less than 0.20 weight percent. As submitted earlier in its December 6, 2007 Response, column 2, line 57, of Nakaoka discloses

that the zeolite Y *per se* (not the total catalyst composition) should have a sodium content of less than 0.50%. Nakaoka is therefore only addressing the zeolite itself and is not offering any guidance as to the catalyst composition as a whole. The Examiner nevertheless alleges in his August 18, 2008 final rejection that by combining zeolite having sodium levels less than 0.5 % by weight sodium with matrix such as that described in Examples 4 and 6, one would recognize Nakaoka's composition as having a sodium level within the range recited by Appellants. It is submitted, however, that even if this was so, this inherent feature fails to teach achieving such levels in Appellants' composition, much less teach to lower the sodium content to that expressly recited by Appellants to enhance the function of yet another feature not expressly mentioned by Nakaoka, i.e., a Lewis acid component. Indeed, the express teaching by Nakaoka is limited to the zeolite Y itself, not the complete composition containing the zeolite Y. The Examiner's argument with respect to the sodium levels is therefore flawed for the same reasons discussed above with respect to Lewis acidity. Again, the argument relies on, by the Examiner's own admission, an inherent and undisclosed possibility. While such a position may potentially be relevant if the rejection was based on lack of novelty under

35 USC 102, such a position would not be proper in an argument that such a feature would obvious under 35 USC 103(a) to use in a different composition all together. *See In re Shetty*, 195 USPQ 753 (C.C.P.A. 1977).

As summary, Nakaoka is disclosing a hydroprocessing catalyst composition that has a size and composition typical for that application. Nakaoka is therefore not suggesting utilizing catalyst in any form other than that illustrated in its Example 1. Nakaoka's use of zinc or nickel is only suggestive for its hydrogenation properties, and there is no basis in Nakaoka that those metals should be applied to an FCC catalyst for their alleged Lewis acidity property. Indeed, there is evidence that suggests away from using Nakaoko's catalyst for a FCC catalyst. Since the Office Action also acknowledges that Nakaoka does not expressly teach the presence of Lewis acidity, Nakaoka cannot suggest the advantage of preparing a Lewis acid-component containing catalyst for reducing gasoline sulfur in a FCC catalyst composition having the particle sizes recited in claim 1, much less suggest to one of ordinary skill to manipulate  $\text{Na}_2\text{O}$  of the catalyst composition as a whole to levels of 0.20% by weight or less to improve gasoline sulfur reduction.

Chen

The Examiner's reliance on Chen goes no further in teaching one of ordinary skill to modify or otherwise select certain teachings in Nakaoka to arrive at Appellants' invention. Chen's invention relates to a cracking reaction in which methanol is used as a coreactant. A small amount of very fine zeolite is used as the catalyst. The general goal of Chen's patent is to protect the zeolite from adsorption of contaminants present during the reaction, and Chen discovered that mixing methanol with the zeolite acted as protectant for the zeolite. Chen's Abstract, column 5, lines 14-16. and Figure 1 shows that catalyst is used once in the reactor and then exits Chen's process as waste.

Chen describes using "finely divided" zeolite crystal in his process, and Column 4, line 38, describes the catalyst as having a mean particle size of  $3 \times 10^{-4}$  cm, which is equivalent to 3 microns. It is submitted that Chen does not teach combining the zeolite with any other materials such as inorganic matrix and Lewis Acid components to form a particulate in the size range recited in claim 1. Indeed, Chen would have no need for materials other than zeolite because the catalyst is discharged after its first use. It therefore is not seen how Chen teaches modifying a catalyst

taught by Nakaoka, much less teaching one to modify it to a catalyst composition, size, and form used in a FCC process.

In light of the nature of Chen's invention as described above, it is submitted that Chen's text (column 1, lines 27-33) referenced in the Office Action, i.e., catalyst having sizes of 1 to 140 microns, is not reflective of what one of ordinary skill would glean from Chen. Indeed, Chen states in the very same section of text that zeolites have also been used in fixed bed catalysts that have particles ***no smaller*** than 1/25 inch, which is equivalent to about 1 millimeter or greater. The Examiner has offered no rationale why one of ordinary skill in the art would adopt the former over the latter to modify Nakaoka. Indeed, it is equally and likely more plausible that one of ordinary skill in the art would, in light of Nakaoka, take precautions to maintain the millimeter size of catalyst taught by Nakaoka, because Chen confirms that such fixed bed catalysts should be ***no smaller than 1000 microns***. Chen therefore suggests away from modifying fixed bed catalysts such as Nakaoka to be of the size now recited in claim 1. It is submitted that to construe Chen otherwise amounts to the Examiner failing to consider the prior art as a whole. It is impermissible within the framework of 35 USC 103(a) to pick and

choose from any one reference only so much of it as will support a given position, to the exclusion of other parts necessary to the full appreciation of what such reference fairly suggests to one of ordinary skill. *See In re Wesslau*, 147 U.S.P.Q. 391, 393 (C.C.P.A. 1965).

The Examiner also takes the position in the August 18, 2008 final rejection that Geldart, Appendix A, confirms that Chen and Nakaoka suggests particles that are fluidizable in FCC processes. Appellants respectfully disagree for reasons stated earlier. Briefly, Nakaoka discloses and teaches millimeter sized catalysts for hydroprocessing. Chen teaches utilizing very fine zeolite crystals of 3 micron size for use in a “one pass” reaction that does not require any of the features suitable for surviving the process of regeneration and recirculation to a reactor. The Examiner’s position, moreover, completely disregards Geldart’s description that class D particles, e.g., those in the size range of Nakaoka’s catalyst, would require far more gas than required for chemical operation. Geldart is also completely silent on modifying millimeter sized hydroprocessing catalyst to maximize its efficiency as a FCC catalyst.



## **Conclusion**

Accordingly, it is submitted that the claims as appended hereto are patentable and Appellants request reversal of the Examiner's rejection of claims 1-29 and 33-44 based on Nakaoka and Chen.

Respectfully submitted,

A handwritten signature in black ink, appearing to read 'Charles A. Cross', written in a cursive style.

Charles A. Cross  
Attorney for Appellants  
Reg. No. 32,406

Tel: (410) 531-4518  
Fax: (410) 531-4195  
Email: [charles.a.cross@grace.com](mailto:charles.a.cross@grace.com)  
W. R. Grace & Co.-Conn.  
7500 Grace Drive  
Columbia, Maryland 21044  
Charge: DAV/FCC

## **Appendix**

### **1. Claims Section**

1. (Rejected) A cracking catalyst composition capable of being maintained in a fluidized state within a fluid cracking catalyst unit used in cracking hydrocarbon feedstock containing organic sulfur-containing compounds, the cracking catalyst composition comprising

- (a) Zeolite;
- (b) Lewis Acid-containing component; and
- (c) inorganic oxide matrix;

wherein the cracking catalyst composition further comprises 0.20 percent by weight  $\text{Na}_2\text{O}$  or less, and wherein the average particle size of the cracking catalyst composition is in the range of 20 to 150 microns.

2. (Rejected) The composition of Claim 1 wherein the composition comprises 0.15 percent by weight  $\text{Na}_2\text{O}$  or less.

3. (Rejected) The composition of Claim 1 wherein the composition comprises 0.10 percent by weight  $\text{Na}_2\text{O}$  or less.

4. (Rejected) The composition of Claim 1 wherein the zeolite (a) comprises 0.5 percent by weight  $\text{Na}_2\text{O}$  or less.

5. (Rejected) The composition of Claim 1 wherein the zeolite (a) comprises 0.3 percent by weight  $\text{Na}_2\text{O}$  or less.

6. (Rejected) The composition of Claim 1 wherein the zeolite (a) comprises 0.1 percent by weight  $\text{Na}_2\text{O}$  or less.

7. (Rejected) The composition of Claim 1 wherein the Lewis Acid-containing component (b) comprises 0.1 percent by weight  $\text{Na}_2\text{O}$  or less.

8. (Rejected) The composition of Claim 1 wherein the zeolite is a Y-type zeolite selected from the group consisting of HY, USY, REY, REUSY, CREY, CREUSY, MgUSY, ZnUSY, MnUSY-type zeolites and mixtures thereof.

9. (Rejected) The composition of Claim 1 wherein the zeolite is a Y-type zeolite selected from the group consisting of USY, REY, REUSY, CREY, CREUSY and mixtures thereof.

10. (Rejected) The composition of Claim 2 wherein the zeolite is a Y-type zeolite selected from the group consisting of USY, REY, REUSY, CREY, CREUSY and mixtures thereof.

11. (Rejected) The composition of Claim 4 wherein the zeolite is a Y-type zeolite selected from the group consisting of USY, REY, REUSY, CREY, CREUSY and mixtures thereof.

12. (Rejected) The composition of Claim 5 wherein the zeolite is a Y-type zeolite selected from the group consisting of USY, REY, REUSY, CREY, CREUSY and mixtures thereof.

13. (Rejected) The composition of Claim 1 wherein the zeolite has an average unit cell size of from about 24.25 to 24.50Å.

14. (Rejected) The composition of Claim 1 wherein the zeolite has an average unit cell size of from about 24.5 to 24.7Å.

15. (Rejected) The composition of Claim 1 wherein the Lewis Acid-containing component (b) comprises alumina.

16. (Rejected) The composition of Claim 1, wherein the Lewis Acid-containing component (b) comprises alumina and at least one metal selected from the group consisting of Ni, Cu, Zn, Ag, Cd, In, Sn, Hg, Ti, Pb, Bi, B, Mn, Ga and mixtures thereof, wherein said at least one metal is present as an oxide, as a cation or is in its zero valence state.

17. (Rejected) The composition of Claim 1 wherein the Lewis Acid-containing component (b) has a metal selected from the group consisting of Zn, Ti, Co, Mo, Fe and mixtures thereof, wherein said metal is present as an oxide, as a cation or is in its zero valence state.

18. (Rejected) The composition of Claim 15 wherein the metal of the Lewis Acid-containing component (b) further comprises Zn.

19. (Rejected) The composition of Claim 2, wherein the Lewis Acid-containing component (b) comprises alumina and at least one metal selected from the group consisting of Ni, Cu, Zn, Ag, Cd, In, Sn, Hg, Ti, Pb, Bi, B, Mn, Ga and mixtures thereof, wherein said at least one metal is present as an oxide, as a cation or is in its zero valence state.

20. (Rejected) The composition of Claim 2 wherein the Lewis Acid-containing component (b) has a metal selected from the group consisting of Zn, Ti, Co, Mo, Fe and mixtures thereof, wherein said metal is present as an oxide, as a cation or is in its zero valence state.

21. (Rejected) The composition of Claim 2 wherein the metal of the Lewis Acid-containing component (b) comprises Zn.

22. (Rejected) The composition of Claim 7, wherein the Lewis Acid-containing component (b) comprises alumina and at least one metal selected from the group consisting of Ni, Cu, Zn, Ag, Cd, In, Sn, Hg, Ti, Pb, Bi, B, Mn, Ga and mixtures thereof, wherein said at least one metal is present as an oxide, as a cation or is in its zero valence state.

23. (Rejected) The composition of Claim 15 wherein the alumina has a particle size of from 20 to 150 $\mu$  and a surface area of from 30 to 400 m<sup>2</sup>/g.

24. (Rejected) The composition of Claim 15 wherein the zeolite (a) further contains rare earth.

25. (Rejected) The composition of Claim 1 wherein the composition comprises at least 3% by weight Lewis Acid-containing component (b).

26. (Rejected) The composition of Claim 25 wherein the Lewis Acid-containing component (b) is a Lewis Acid metal cation exchanged on zeolite (a).

27. (Rejected) The composition of Claim 1 wherein the composition comprises from about 3 to about 75 weight percent of component (b).

28. (Rejected) The composition of Claim 1 wherein the composition comprises 30 to 75 weight percent of component (b).

29. (Rejected) The composition of Claim 27 wherein zeolite (a) is a Y-type zeolite having a sodium content of 0.3% by weight  $\text{Na}_2\text{O}$  or less, and the composition has a kinetic conversion activity of at least about 2.

30. (Cancelled).

31. (Rejected) The composition of Claim 1 wherein the composition comprises a blend of least two separate particles, one

particle comprising zeolite (a) and inorganic oxide matrix (c) and the other particle comprising Lewis Acid-containing component (b).

32. (Rejected) The composition of Claim 31 wherein the Lewis Acid-containing component (b) comprises alumina and at least one metal selected from the group consisting of Ni, Cu, Zn, Ag, Cd, In, Sn, Hg, Ti, Pb, Bi, B, Mn, Ga and mixtures thereof, wherein said at least one metal is present as an oxide, as a cation or is in its zero valence state.

33. (Rejected) The composition according to Claim 32 wherein the composition comprises 0.15% by weight  $\text{Na}_2\text{O}$  or less.

34. (Rejected) The composition according to Claim 32 wherein the zeolite (a) comprises 0.3% by weight  $\text{Na}_2\text{O}$  or less.

35. (Rejected) The composition according to Claim 32 wherein the Lewis Acid-containing component comprises 0.10% by weight  $\text{Na}_2\text{O}$  or less.

36. (Rejected) The composition according to Claim 34 wherein the composition comprises 0.15% by weight  $\text{Na}_2\text{O}$  or less.

37. (Rejected) The composition of Claim 31 wherein Lewis Acid-containing component (b) comprises alumina and Zn, wherein said Zn is present as an oxide or is in its zero valence state.

38. (Rejected) The composition of Claim 31 wherein the composition has a kinetic conversion activity of at least about 2.

39. (Rejected) The composition of Claim 32 wherein the composition has a kinetic conversion activity of at least about 2.

40. (Rejected) The composition of Claim 1 further comprising vanadium.

41. (Rejected) The composition of Claim 31 further comprising vanadium.

42. (Rejected) The composition of Claim 32 further comprising vanadium.

43. (Cancelled)

44. (Rejected) The composition of Claim 1 where in the average particle size of the composition is in the range of 60 to 90 microns.

45. (Withdrawn) An improved process for catalytic cracking of hydrocarbon feedstock which contains organic sulfur compounds comprising contacting in a catalytic cracking reactor of a fluid catalyst cracking unit an inventory of fluid cracking catalyst composition, removing the liquid and gaseous product streams from said reactor, transferring a portion of the inventory to regenerators of said unit



to remove contaminants before returning same to the reactor, removing a portion of the inventory from the unit while replacing same with fresh catalyst composition to provide an equilibrium state of said inventory, the improvement comprising (1) adding to the inventory of fluid cracking catalyst composition in the unit a fresh cracking catalyst composition comprising (a) zeolite, and (b) Lewis Acid-containing component, wherein the cracking catalyst composition further comprises 0.20 percent by weight  $\text{Na}_2\text{O}$  or less, and (2) recovering a liquid product having a boiling point of up to about  $220^\circ\text{C}$ , said liquid product having a sulfur content that is at least 15 weight percent lower than that attained by a composition composed of the same zeolite catalyst without Lewis Acid-containing component (b).

46. (Withdrawn) An improved process according to Claim 45 wherein the fresh cracking catalyst composition comprises a catalyst according to any one of claims 2-.

47. (Withdrawn) An improved process according to claim 46 wherein said liquid product has a sulfur content that is at least 20% percent lower than that attained by a composition composed of the same zeolite catalyst without Lewis Acid-containing component (b).

48. (Withdrawn) A method of reducing sulfur in gasoline originating from a naphtha stream generated by a fluidized catalytic cracking (FCC) unit having a reaction stage and a regeneration stage process, the method comprising:

- (a) preparing a cracking catalyst composition comprising zeolite and Lewis Acid-containing component wherein the cracking catalyst composition further comprises 0.20 percent by weight  $\text{Na}_2\text{O}$  or less;
- (b) adding the catalyst composition to a catalyst inventory of the FCC unit;
- (c) introducing the catalyst composition to the reaction stage of the FCC unit in amounts sufficient to convert hydrocarbon feed entering the reaction stage of the FCC unit into hydrocarbon products having a sulfur content of at least 15% less than that produced when using a catalyst composition without said Lewis Acid-containing component; and
- (d) recycling the catalyst inventory from (c) to the regeneration stage of the FCC unit to remove coke from the catalyst inventory.

49. (Withdrawn) A method according to Claim 48 wherein the cracking catalyst composition comprises a metal selected from the group consisting of Zn, Ti, Co, Mo, Fe, and mixtures thereof, wherein said metal is present as an oxide, as a cation or is in its zero valence state.

50. (Withdrawn) A method according to Claim 49 wherein the metal is Zn.

51. (Withdrawn) A method according to Claim 48 wherein the Lewis Acid component comprises alumina.

52. (Withdrawn) A method for making a cracking catalyst composition capable of being maintained within a fluid cracking catalyst unit used in cracking hydrocarbon feedstock, the method for making the catalyst comprising:

- (a) selecting a zeolite comprising about 0.5 percent by weight  $\text{Na}_2\text{O}$  or less,
- (b) selecting a Lewis Acid-containing component comprising about 0.1 percent  $\text{Na}_2\text{O}$  or less, and
- (c) combining said zeolite and Lewis Acid-containing component in proportions sufficient to produce a catalyst composition that comprises about 0.2 percent by weight  $\text{Na}_2\text{O}$  or less.

53. (Withdrawn) The method of Claim 52 wherein the catalyst composition produced in (c) comprises 0.15 percent by weight  $\text{Na}_2\text{O}$  or less.

54. (Withdrawn) The method of Claim 52 wherein the catalyst composition produced in (c) comprises 0.10 percent by weight  $\text{Na}_2\text{O}$  or less.

55. (Withdrawn) The method of Claim 52 wherein the zeolite selected in (a) comprises 0.3 percent by weight  $\text{Na}_2\text{O}$  or less.

56. (Withdrawn) The method of Claim 52 wherein the zeolite selected in (a) comprises 0.1 percent by weight  $\text{Na}_2\text{O}$  or less.

57. (Withdrawn) The method of Claim 52 wherein the zeolite selected in (a) is a Y-type zeolite selected from the group consisting of HY, USY, REY, REUSY, CREY, CREUSY, MgUSY, ZnUSY, MnUSY-type zeolites and mixtures thereof.

58. (Withdrawn) The method of Claim 52 wherein the zeolite selected in (a) is a Y-type zeolite selected from the group consisting of USY, REY, REUSY, CREY, CREUSY and mixtures thereof.

59. (Withdrawn) The method of Claim 53 wherein the zeolite selected in (a) is a Y-type zeolite selected from the group

consisting of USY, REY, REUSY, CREY, CREUSY and mixtures thereof.

60. (Withdrawn) The method of Claim 54 wherein the zeolite selected in (a) is a Y-type zeolite selected from the group consisting of USY, REY, REUSY, CREY, CREUSY and mixtures thereof.

61. (Withdrawn) The method of Claim 55 wherein the zeolite selected in (a) is a Y-type zeolite selected from the group consisting of USY, REY, REUSY, CREY, CREUSY and mixtures thereof.

62. (Withdrawn) The method of Claim 56 wherein the zeolite selected in (a) is a Y-type zeolite selected from the group consisting of USY, REY, REUSY, CREY, CREUSY and mixtures thereof.

63. (Withdrawn) The method of Claim 52, wherein the Lewis Acid-containing component selected in (b) comprises alumina and at least one metal selected from the group consisting of Ni, Cu, Zn, Ag, Cd, In, Sn, Hg, Ti, Pb, Bi, B, Mn, Ga and mixtures thereof, wherein said at least one metal is present as an oxide, as a cation or is in its zero valence state.

64. (Withdrawn) The method of Claim 52 wherein the Lewis Acid-containing component selected in (b) comprises a metal selected from the group consisting of Zn, Ti, Co, Mo, Fe and mixtures thereof, wherein said metal is present as an oxide, as a cation or is in its zero valence state.

65. (Withdrawn) The method of Claim 54, wherein the Lewis Acid-containing component selected in (b) comprises alumina and at least one metal selected from the group consisting of Ni, Cu, Zn, Ag, Cd, In, Sn, Hg, Ti, Pb, Bi, B, Mn, Ga and mixtures thereof, wherein said at least one metal is present as an oxide, as a cation or is in its zero valence state.

66. (Withdrawn) The method of Claim 54 wherein the Lewis Acid-containing component selected in (b) comprises a metal selected from the group consisting of Zn, Ti, Co, Mo, Fe and mixtures thereof, wherein said metal is present as an oxide, as a cation or is in its zero valence state.

67. (Withdrawn) The method of Claim 52, wherein the catalyst composition produced in (c) comprises at least about 3% by weight of Lewis Acid-containing component selected in (b).

68. (Withdrawn) The method of Claim 67 wherein the Lewis Acid-containing component is a metal cation produced during an exchange reaction with the zeolite.

69. (Withdrawn) The method of Claim 52 wherein the catalyst composition produced in (c) comprises from about 3 to about 75 weight percent of Lewis Acid-containing component selected in (b).

70. (Withdrawn) The method of Claim 52 wherein the catalyst composition produced in (c) comprises 30 to 75 weight percent of Lewis Acid-containing component selected in (b).

71. (Withdrawn) The method of Claim 67 wherein zeolite selected in (a) is a Y-type zeolite having a sodium content of 0.3% by weight  $\text{Na}_2\text{O}$  or less, and the catalyst composition produced in (c) has a kinetic conversion activity of at least about 2.

2. Claim Support

1. A cracking catalyst composition capable of being maintained in a fluidized state within a fluid cracking catalyst unit {0021} used in cracking hydrocarbon feedstock containing organic sulfur-containing compounds {0001}, the cracking catalyst composition comprising

- (a) zeolite {0022};
- (b) Lewis Acid-containing component {0041}; and
- (c) inorganic oxide matrix {original claim 30}; {0030};

wherein the cracking catalyst composition further comprises 0.20 percent by weight  $\text{Na}_2\text{O}$  or less {0019}; {0032}, and wherein the average particle size of the cracking catalyst composition is in the range of 20 to 150 microns. {original claim 43}; {0030}



3. Evidence Section

- A. "Fluidization Engineering", Second Edition, Buttersworth-Heinemann (1991) pp. 77-79, 93 (also referred to herein as "Geldart").
- B. US 4,705,621 (8 pages).
- C. "Fluid Catalytic Cracking: Science and Technology", (1993), pp. 339-346.

1 P  
156  
165K8  
1991

APPENDIX A

# Fluidization Engineering

SECOND EDITION

**Daizo Kunii**

Fukui Institute of Technology  
Fukui City, Japan

**Octave Levenspiel**

Chemical Engineering Department  
Oregon State University  
Corvallis, Oregon

**Butterworth-Heinemann**

Boston London Singapore Sydney Toronto Wellington

Copyright © 1991 by Butterworth-Heinemann, a division of Reed Publishing (USA) Inc. All rights reserved.

No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording, or otherwise, without the prior written permission of the publisher.

Recognizing the importance of preserving what has been written, it is the policy of Butterworth-Heinemann to have the books it publishes printed on acid-free paper, and we exert our best efforts to that end.

**Library of Congress Cataloging-in-Publication Data**

Kunii, Daizo, 1923-

Fluidization engineering / Daizo Kunii, Octave Levenspiel.  
—2nd ed.

p. cm.—(Butterworth-Heinemann series in chemical engineering)

ISBN 0-409-90233-0

I. Fluidization. I. Levenspiel, Octave. II. Title.  
III. Series.

TP156.F65K8 1991

660'.284292—dc20

90-31800

**British Library Cataloguing in Publication Data**

Kunii, Daizo

Fluidization engineering.

1. Chemical engineering. Fluidisation

I. Title II. Levenspiel, Octave  
660.2842

ISBN 0-409-90233-0

Butterworth-Heinemann  
80 Montvale Avenue  
Stoneham, MA 02180

10 9 8 7 6 5 4 3 2 1

Printed in the United States of America

Numerous attempts have been made to devise a criterion to predict the mode of fluidization and the transition from one mode to another. Wilhelm and Kwauk [42] were the first. They considered interparticle forces in the vicinity of bubbles and proposed using the Froude number as the criterion for flow transition. Romero and Johanson [43] extended this idea to four dimensionless groups, which included the Reynolds number and the Froude number. Zenz [44], taking a different approach, presented an empirical plot of bed voidage versus  $\rho_s/\rho_g$  with particle size as parameter. Criteria for indicating when bubbles would form, based on stability theory as applied to growth rate of pressure disturbances in the bed, were proposed by three groups [45–47]. Others [48,49], opposed to these criteria, assumed that bubbles were always present in fluidized beds but were not observable below a certain size. Even the existence of shock waves was proposed as a criterion for transition from nonbubbling to bubbling behavior [50].

Geldart [51] approached this question in a different way. He focused on the characteristics of the particles that make them fluidize in one way or another. His approach is simple, has great generalizing power, and is very useful.

### The Geldart Classification of Particles

By carefully observing the fluidization of all sorts and sizes of solids, Geldart [51] came up with four clearly recognizable kinds of particle behavior. From smallest to largest particle, they are as follows:

- Group C: cohesive, or very fine powders. Normal fluidization is extremely difficult for these solids because interparticle forces are greater than those resulting from the action of gas. Face powder, flour, and starch are typical of these solids.
- Group A: aeratable, or materials having a small mean particle size and/or low particle density ( $< \sim 1.4 \text{ g/cm}^3$ ). These solids fluidize easily, with smooth fluidization at low gas velocities and controlled bubbling with small bubbles at higher gas velocities. FCC catalyst is representative of these solids.
- Group B: sandlike, or most particles of size  $40 \mu\text{m} < \bar{d}_p < 500 \mu\text{m}$  and density  $1.4 < \rho_s < 4 \text{ g/cm}^3$ . These solids fluidize well with vigorous bubbling action and bubbles that grow large.
- Group D: spoutable, or large and/or dense particles. Deep beds of these solids are difficult to fluidize. They behave erratically, giving large exploding bubbles or severe channeling, or spouting behavior if the gas distribution is very uneven. Drying grains and peas, roasting coffee beans, gasifying coals, and some roasting metal ores are such solids, and they are usually processed in shallow beds or in the spouting mode.

Geldart's classification is clear and easy to use and is readily displayed in Fig. 9 for air fluidization at ambient conditions and for  $u_o$  less than about  $10u_{mf}$ . For any solid of known density  $\rho_s$  and mean particle size  $\bar{d}_p$ , this graph shows the type of fluidization to be expected. This grouping of solids is widely used today, with the solids simply called *Geldart A solids*, and so forth. We follow this practice here.

We now discuss the distinctive characteristics of solids in these groupings.

**Geldart C Particles.** In small-diameter beds Geldart C particles, which are difficult to fluidize, tend to rise as a plug of solids, whereas in larger-

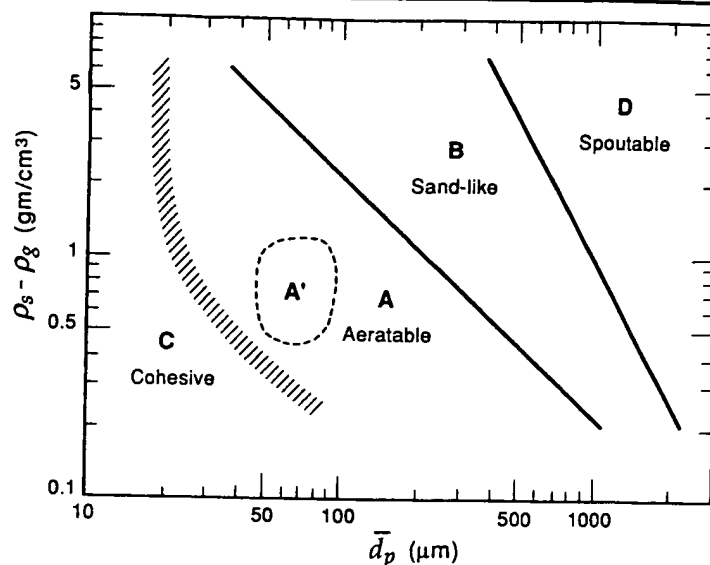


FIGURE 9

The Geldart classification of particles for air at ambient conditions; adapted from Geldart [51]. Region A': Range of properties for well-behaved FCC catalyst; from Miyauchi et al. [11].

diameter beds channels form from distributor to bed surface with no fluidization of solids. These particles have been studied by Geldart [52].

One way of processing these solids is to introduce them into a bed of the same material but of larger size, preferably Geldart **B**. Even though the fines are very small, they are not entrained immediately, but may stay in the bed an average of several minutes. This usually is long enough for a physical or chemical transformation of these solids.

**Geldart A Particles.** When these solids are fluidized, the bed expands considerably before bubbles appear, as mentioned earlier. At gas velocities higher than  $u_{mb}$ , the bed shifts to the bubbling mode, characterized as follows:

- Gas bubbles rise more rapidly than the rest of the gas, which percolates through the emulsion.
- These gas bubbles appear to split and coalesce frequently as they rise through the bed. There is a maximum bubble size, usually less than 10 cm, even in a large bed.
- Internals do not appreciably improve fluidization.
- Gross circulation of solids occurs even when only a few bubbles are present. This circulation is especially pronounced in large beds.
- When bubbles grow to the vessel diameter, they turn into axial slugs (see Fig. 1.1).

Fines act as a lubricant to make it easier to fluidize the bed. Thus, the ratio  $u_{mb}/u_{mf}$  increases with added fines, namely  $P_{45} \mu m$ , as indicated by Eq. (27). The size distribution of typical Geldart A solids that fluidize well is shown in Fig. 2.

**Geldart B Particles.** In beds of Geldart **B** solids, bubbles form as soon as the gas velocity exceeds  $u_{mf}$ . Thus,  $u_{mb}/u_{mf} \cong 1$ , as opposed to Geldart **A** solids. At higher gas velocities, the bed behaves as follows:

- Small bubbles form at the distributor and grow and coalesce as they rise through the bed.
- Bubble size increases roughly linearly with distance above the distributor and excess gas velocity,  $u_o - u_{mf}$ .
- Bubble size is roughly independent of mean particle size.
- Vigorous bubbling encourages the gross circulation of solids.

The majority of gas-solid reactions, metallurgical and others, are run in this regime because the mean size and size distribution of feed particles are usually determined by the upstream processing of the raw materials.

**Geldart D Particles.** Fluidized beds of Geldart **D** solids have the following properties:

- Bubbles coalesce rapidly and grow to large size.
- Bubbles rise more slowly than the rest of the gas percolating through the emulsion.
- The dense phase has a low voidage.
- When the bubble size approaches the bed diameter, flat slugs are observed (see Fig. 1.1).
- These solids spout easily, whereas Geldart **B** solids do not.

Large particle beds are usually undesirable for physical or chemical operations. However, in some industries, for instance, in processing agricultural products, in chemical agglomeration, and in the reaction of composite pellets, one cannot avoid this.

An enormous amount of gas is needed to fluidize these solids, often far more than required for the physical or chemical operation. In such situations, one may want to use spouted beds, since they need much less gas.

Bubbling can be made to occur with these solids if the bed is shallow, has sufficient diameter, and the gas velocity is not much more than  $u_{mf}$ . To avoid slugging, especially at onset of fluidization, the vessels are sometimes designed with a larger-diameter upper section, as shown in Figs. 2.1(a) and 2.16(b).

As shown in Fig. 2.3, in some operations two modes of fluidization are combined (i.e., spouting and bubbling) to get better contacting.

**Extensions of the Geldart Chart.** Figure 9 was originally proposed for beds only at ambient conditions. Further studies have led to a number of proposed modifications and refinements. For example, an **AC** classification for particles in the uncertain transition region between Geldart **A** and Geldart **C** solids has been proposed. These solids flow well when fluidized (type **A** influence), but they permanently defluidize on any horizontal surface and thus block or plug horizontal pipes (type **C** influence).

Another area of study seeks to locate more clearly the boundary between regions. This should depend not only on densities and mean solid size (see Fig. 9) but also on  $u_o/u_{mf}$ , gas properties, and the size distribution of solids. Grace [53] presents the latest findings in this area.

We consider the whole question of flow regime in a much broader context in the last section of this chapter, where a generalized flow diagram is displayed.

15. S.P. Babu, B. Shah, and A. Talwalkar, *AIChE Symp. Ser.*, **74**(176), 176 (1978).
16. J.R. Grace, in *Handbook of Multiphase Systems*, G. Hetsroni, ed., p. 8-1, Hemisphere, Washington, D.C., 1982.
17. D.C. Chitester et al., *Chem. Eng. Sci.*, **39**, 253 (1984).
18. J.P. Couderc, in *Fluidization*, 2nd ed., J.F. Davidson et al., eds., Chap. 1, Academic Press, New York, 1985.
19. W.C. Yang et al., *AIChE J.*, **31**, 1085 (1985).
20. T. Shirai, *Fluidized Beds*, Kagaku-Gijutsu-Sha, Kanazawa, 1958.
21. S. Morooka, M. Nishinaka, and Y. Kato, *Kagaku Kogaku*, **37**, 485 (1973).
22. D. Geldart and A.R. Abrahamsen, *Powder Technol.*, **19**, 133 (1978); **26**, 34, 47 (1980); in *Fluidization III*, J.R. Grace and J.M. Matsen, eds., p. 453, Plenum, New York, 1980.
23. E.F. Brooks and T.J. Fitzgerald, "Aggregation and Fluidization Characteristics of a Fibrous Carbon," paper delivered at annual meeting of American Institute of Chemical Engineers, November 1985.
24. T. Varadi and J.R. Grace, in *Fluidization*, J.F. Davidson and D.L. Keairns, eds., p. 50, Cambridge Univ. Press, New York, 1978.
25. J.R.F. Guedes de Carvalho, D.F. King, and D. Harrison, in *Fluidization*, J.F. Davidson and D.L. Keairns, eds., p. 59, Cambridge Univ. Press, New York, 1978; D.F. King and D. Harrison, *Trans. Inst. Chem. Eng.*, **60**, 26 (1982); J.R.F. Guedes de Carvalho, *Chem. Eng. Sci.*, **36**, 413 (1981).
26. M.E. Crowther and J.C. Whitehead, in *Fluidization*, J.F. Davidson and D.L. Keairns, eds., p. 65, Cambridge Univ. Press, New York, 1978.
27. P.N. Rowe et al., in *Fluidization IV*, D. Kunii and R. Toei, eds., p. 53, Engineering Foundation, New York, 1983.
28. L.E.L. Sobreiro and J.L.F. Monteiro, *Powder Technol.*, **33**, 95 (1982).
29. A.W. Weimer and G.J. Quaderer, *AIChE J.*, **31**, 1019 (1985); A.W. Weimer, *AIChE J.*, **32**, 877 (1986).
30. W.C. Yang et al., *AIChE J.*, **31**, 1086 (1985).
31. T. Mii, K. Yoshida, and D. Kunii, *J. Chem. Eng. Japan*, **6**, 100 (1973).
32. M. Avedesian and J.F. Davidson, *Trans. Inst. Chem. Eng.*, **51**, 121 (1973).
33. B. Singh, G.R. Rigby, and T.G. Callcott, *Trans. Inst. Chem. Eng.*, **51**, 93 (1973).
34. A. Desai, H. Kikukawa, and A.H. Pulsifer, *Powder Technol.*, **16**, 143 (1977).
35. M.A. Doheim and C.N. Collinge, *Powder Technol.*, **21**, 289 (1978).
36. G.H. Hong et al., *Kagaku Kogaku Ronbunshu*, **6**, 557 (1980).
37. K. Svoboda and M. Hartman, *Ind. Eng. Chem. Process Des. Dev.*, **20**, 319 (1981).
38. J.S.M. Botterill, Y. Teoman, and K.R. Yuregir, *Powder Technol.*, **31**, 101 (1982); J.S.M. Botterill and Y. Teoman, in *Fluidization III*, J.R. Grace and J.M. Matsen, eds., p. 93, Plenum, New York, 1980.
39. R. Yamazaki, G.H. Hong, and G. Jimbo, in *Fluidization IV*, D. Kunii and R. Toei, eds., p. 121, Engineering Foundation, New York, 1983; R. Yamazaki, N. Ueda, and G. Jimbo, *J. Chem. Eng. Japan*, **19**, 251 (1986).
40. K. Kitano et al., *Kagaku Kogaku Ronbunshu*, **12**, 354 (1986).
41. M.J. Gluckman, J. Yerushalmi, and A.M. Squires, in *Fluidization Technology*, D.L. Keairns, ed., vol. 2, p. 395, McGraw-Hill, New York, 1976.
42. R.H. Wilhelm and M. Kwauk, *Chem. Eng. Prog.*, **44**, 201 (1948).
43. J.B. Romero and L.N. Johanson, *Chem. Eng. Prog. Symp. Ser.*, **58**(38), 28 (1962).
44. F.A. Zenz, *Petrol. Refiner*, **36**, 321 (1957).
45. R. Jackson, *Trans. Inst. Chem. Eng.*, **41**, 13 (1963).
46. O. Molerus, in *Proc. Int. Symp. on Fluidization*, A.A.H. Drinkenburg, ed., p. 134, Netherlands Univ. Press, Amsterdam, 1967.
47. R.L. Pigford and T. Baron, *Ind. Eng. Chem. Fundamentals*, **4**, 81 (1965).
48. D. Harrison, J.F. Davidson, and J.W. de Kock, *Trans. Inst. Chem. Eng.*, **39**, 202 (1961).
49. H.C. Simpson and B.W. Rodger, *Chem. Eng. Sci.*, **16**, 153 (1961).
50. J. Verloop and P.M. Heertjes, *Chem. Eng. Sci.*, **25**, 825 (1970).
51. D. Geldart, *Powder Technol.*, **7**, 285 (1973); **19**, 133 (1978).
52. D. Geldart, *Chem. Eng. Sci.*, **39**, 1481 (1984); **40**, 653 (1985).
53. J.R. Grace, *Can. J. Chem. Eng.*, **64**, 353 (1986).
54. A. Haider and O. Levenspiel, *Powder Technol.*, **58**, 63 (1989).
55. R. Turton and N.N. Clark, *Powder Technol.*, **53**, 27 (1987).
56. P.H. Pinchbeck and F. Popper, *Chem. Eng. Sci.*, **6**, 57 (1956).
57. K.P. Lanneau, *Trans. Inst. Chem. Eng.*, **38**, 125 (1960).
58. P.W.K. Kehoe and J.F. Davidson, *Inst. Chem. Eng. Symp. Ser.*, **33**, 97 (1971).
59. L. Carotenuto, S. Crescitelli, and G. Donsi, *Quad. Ing. Chim. Ital.*, **10**, 185 (1974); S. Crescitelli et al., CHISA Conference, 1 (1978).
60. W.J. Thiel and O.E. Potter, *AIChE J.*, **24**, 561 (1978).

# United States Patent [19]

Penick

[11] Patent Number: 4,705,621  
[45] Date of Patent: Nov. 10, 1987

## [54] CATALYTIC REACTOR SYSTEM WITH CROSSCURRENT LIQUID AND GASFLOW

[75] Inventor: Joe E. Penick, Princeton, N.J.

[73] Assignee: Mobil Oil Corporation, New York, N.Y.

[21] Appl. No.: 714,776

[22] Filed: Mar. 22, 1985

[51] Int. Cl.<sup>4</sup> ..... B01J 8/08

[52] U.S. Cl. .... 208/146; 261/94;  
261/95; 422/211; 422/220

[58] Field of Search ..... 422/211, 212, 216, 218,  
422/220; 261/94, 95; 208/146, 166

## [56] References Cited

### U.S. PATENT DOCUMENTS

2,500,235 3/1950 Beckberger .  
2,913,404 11/1959 Lieffers et al. .... 202/166  
3,186,935 6/1965 Vaell ..... 208/59  
3,296,775 1/1967 Squires ..... 55/98  
3,533,754 10/1970 Hallman .  
3,549,295 12/1970 de Galocsy et al. .... 165/106  
3,898,049 8/1975 Burroughs et al. .... 208/146

4,033,727 7/1977 Vautrain ..... 208/146  
4,126,539 11/1978 Derr et al. .  
4,169,879 10/1979 Descoins et al. .... 422/220  
4,568,524 2/1986 Peirine ..... 422/218  
4,588,560 5/1986 Degnan et al. .... 422/211

### FOREIGN PATENT DOCUMENTS

778776 11/1980 U.S.S.R. .... 422/220

Primary Examiner—Barry S. Richman  
Assistant Examiner—William R. Johnson  
Attorney, Agent, or Firm—Alexander J. McKillop;  
Michael G. Gilman; L. G. Wise

## [57] ABSTRACT

A crossflow reactor and operating technique provides a porous body of contact solids, such as a fixed catalyst bed, contained in a sloping configuration. Liquid, such as hydrocarbon oil, to be treated is applied to the bed surface and flows by gravity through the porous solid. Reactant gas flows transverse to the liquid, providing a horizontal component to the liquid to improve contact efficiency.

11 Claims, 4 Drawing Figures

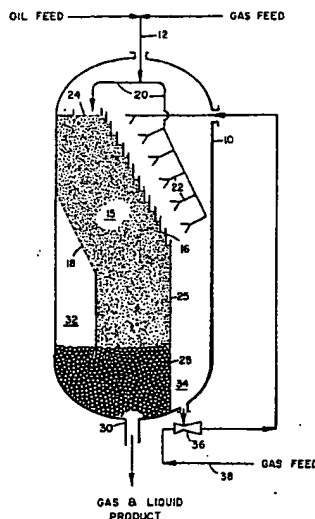
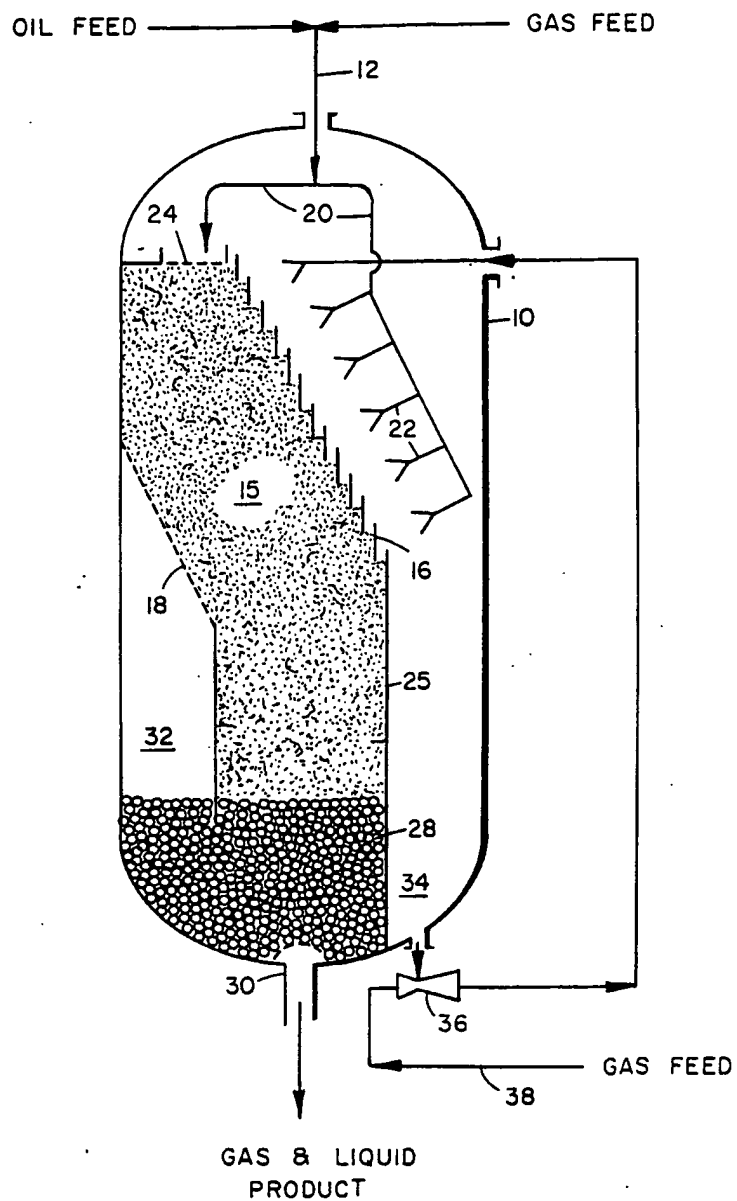




FIG. 1



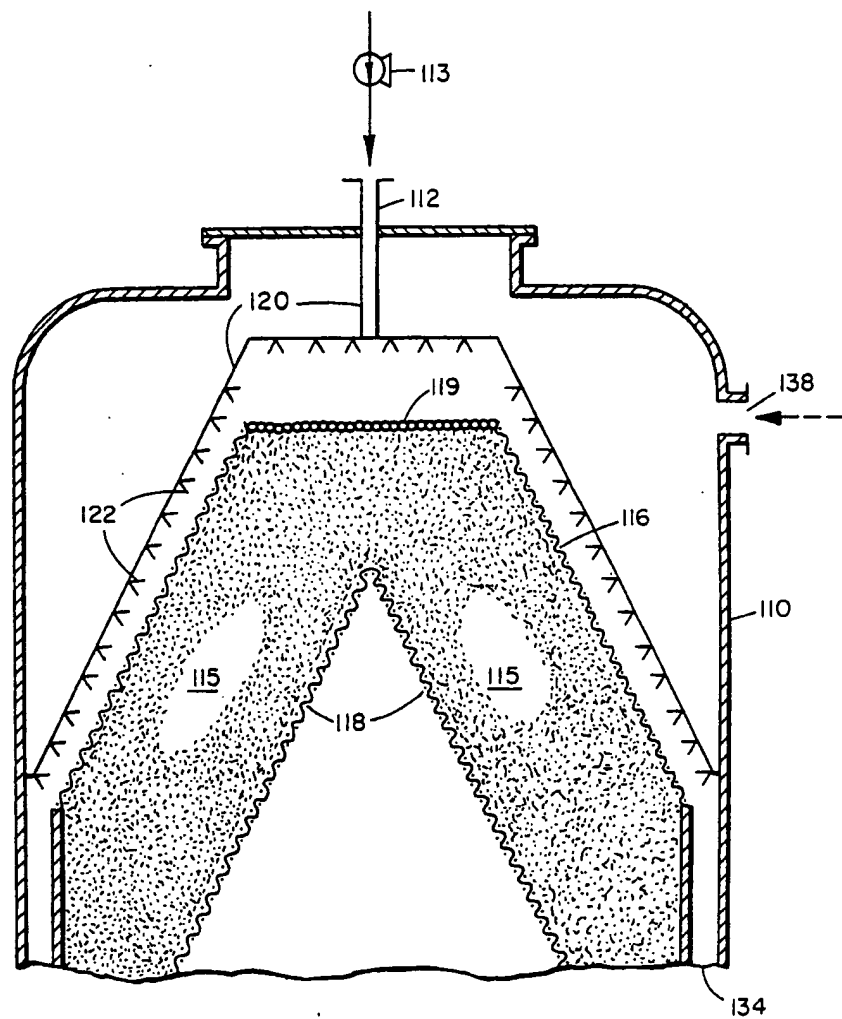


FIG. 2

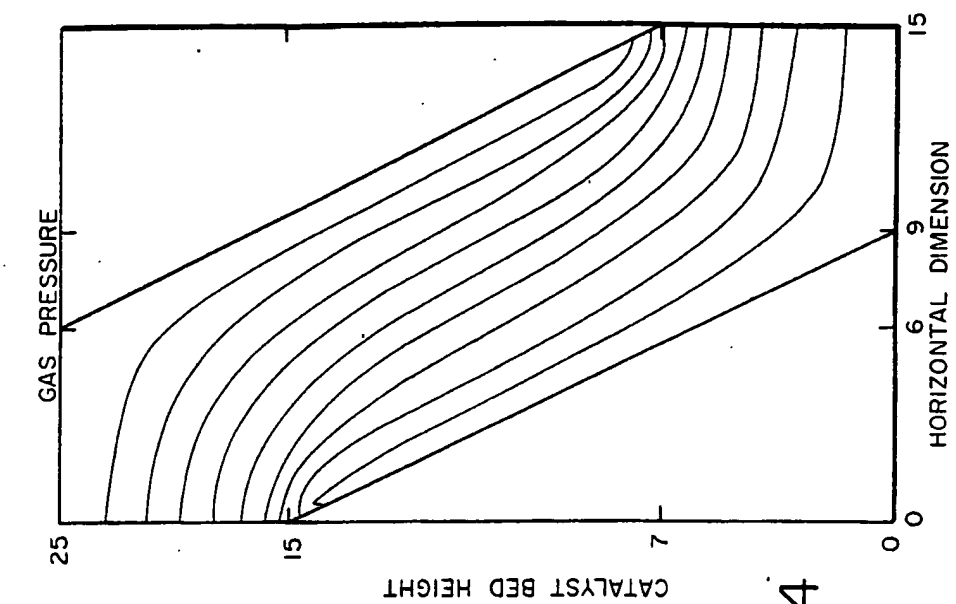


FIG. 3

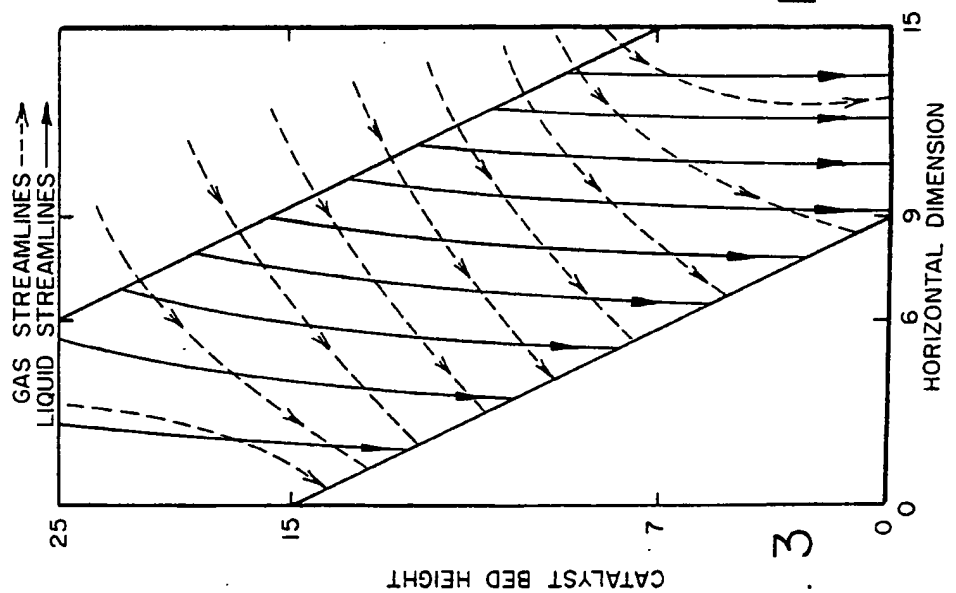


FIG. 4

## CATALYTIC REACTOR SYSTEM WITH CROSSCURRENT LIQUID AND GASFLOW

### BACKGROUND OF THE INVENTION

This invention relates to catalytic reactor operation wherein a liquid phase is treated with a gaseous reactant. In particular it relates to a technique for contacting multi-phase reactants in a fixed porous catalyst bed under continuous operating conditions, including methods and apparatus for controlling transverse fluid flow in the reactor.

Chemical reactions between liquid and gaseous reactants present difficulties in obtaining intimate contact between phases. Such reactions are further complicated when the desired reaction is catalytic and requires contact of both fluid phases with a solid catalyst. In the operation of conventional co-current multiphase reactors, the gas and liquid tend to travel different flow paths. The gas phase flows in the direction of least pressure resistance; whereas the liquid phase flows by gravity in a trickle path over and around the catalyst particles. Channel flow and gas frictional drag tend to make the liquid flow non-uniformly, thus leaving portions of the catalyst bed underutilized due to lack of adequate wetting.

Various attempts have been made to avoid maldistribution, such as the provision of multiple layers of catalyst with interlayered redistributors located along the reactor longitudinal axis. Numerous multi-phase reactor systems have been developed wherein a fixed porous bed of solid catalyst is retained in a reactor. Typically, fixed bed reactors have been arranged with the diverse phases being passed concurrently over the catalyst, for instance as shown in U.S. Pat. Nos. 4,126,539 (Derr et al), 4,235,847 (Scott), 4,283,271 (Garwood et al), and 4,396,538 (Chen et al). Other known techniques for contacting liquid-gas mixtures with solid catalysts include slurry catalyst, ebullated bed, crosscurrent and countercurrent systems, such as disclosed in U.S. Pat. Nos. 2,717,202, 3,186,935, 4,221,653, and 4,269,805. The above cited patents are incorporated herein by reference.

In the petroleum refining industry, multi-phase catalytic reactor systems have been employed for dewaxing, hydrogenation, desulfurizing, hydrocracking, isomerization and other treatments of liquid feedstocks, especially distillates, lubricants, heavy oil fractions, residuum, etc. In a preferred hydrodewaxing process the catalyst comprises a medium pore siliceous zeolite having a constraint index of about 1 to 12, for example, an acidic ZSM-5 type pentasil aluminosilicate having a silica to alumina mole ratio greater than 12.

While prior reactor systems are satisfactory for certain needs, efficient multi-phase contact has been difficult to achieve for many fixed bed applications. It is an object of the present invention to provide a unique reactor system, including crosscurrent operating techniques and apparatus, for improved treatment of liquid with a gaseous reactant in a reactor containing a porous fixed bed of solid catalyst. It is a further object to provide a technique for operating multi-phase reactors under controlled flow conditions to maintain substantially uniform gas-liquid contact, while minimizing flow maldistribution patterns and providing horizontal gas motion simultaneously with a downwardly gravitating liquid motion.

### SUMMARY OF THE INVENTION

In the process of treating a liquid stream, such as hydrocarbon oil, with a gaseous stream in a contact zone containing a porous bed of contact solids, an improved technique has been discovered for maintaining uniform distribution of liquid and gas phases. An operating method and means are provided for distributing the liquid stream at spaced points across the contact solids at a primary bed surface, while containing the contact solids with the primary bed surface sloping outwardly and downwardly from an upper contact zone toward a lower contact zone by supporting the bed with a foraminous screen, louvered wall or the like.

The primary bed surface faces the distributed liquid stream to admit at least a portion of the liquid stream into the porous bed through the primary bed surface, while permitting unadmitted liquid to flow by gravity downwardly across the sloping primary surface, and maintaining gravity flow of liquid through said porous bed. A second foraminous partition means is provided for containing the contact solids with a secondary bed surface substantially parallel to the primary bed surface. By introducing the gaseous stream to the contact zone through the primary bed surface and directing the gas flow toward the secondary bed surface transverse to liquid flow, a horizontal vector is imposed on the liquid flow to drive gravitating liquid across the bed. Outlet means is provided for recovering the treated liquid and gas streams downstream from the porous bed.

These and other features and advantages of the invention will be seen in the following description and drawing.

### THE DRAWING

FIG. 1 is a simplified process diagram showing a vertical reactor with fixed catalyst bed, major flow streams, and distribution elements;

FIG. 2 is a vertical cross-section view of a conical reactor showing a preferred radial gas flow configuration;

FIG. 3 is a graphic plot of a porous catalyst bed section with typical multi-phase streamline flow depicted; and

FIG. 4 is a bed pressure profile showing isobars through the porous bed.

### DESCRIPTION OF PREFERRED EMBODIMENTS

Referring to FIG. 1, a vertical reactor vessel is shown schematically, including a pressurized enclosed reactor shell 10 having top inlet means 12 for liquid and gaseous reactant streams above a porous contact bed 15 of catalyst solids. Catalyst containment means within the reactor vessel retains the fixed porous bed of catalyst particles for multiphase cross-current catalytic treatment. Liquid distributor means 20 is adapted for applying liquid reactant onto a top portion of the catalyst bed through a spaced array of spray nozzles 22 and a top distributor plate 24 above the fixed bed 15.

The bed containment means has rectilinear foraminous walls 16, 18 for admitting and removing reactant gas in crosscurrent flow transverse to gravitational liquid flow, including at least one foraminous containment surface sloping outwardly from the porous catalyst bed on one side thereof. The spray nozzles 22 provide liquid projection means for distributing reactant liquid onto the outwardly sloping primary bed surface

16, whereby at least a portion of liquid reactant passes through the foraminous surface into the porous catalyst bed 15. While the primary sloping wall 16 is depicted as a series of overlapping parallel louvers, a grid plate, perforated sheet, woven screen or similar containment means may be employed for either the top primary surface 16 or the parallel bottom secondary surface 18. A bottom enclosed vertical reaction zone 25 may be disposed to receive reaction products from the upper contact zone 15. Vertical height of zone 25 should be at least as great as the bed thickness between foraminous walls in the upper reaction zone 15 to prevent shunting of fluids. The entire bed may be supported at the bottom of the reactor shell by inert ceramic balls 28. Outlet 30 provides means for recovering catalytically treated liquid and depleted gas below the porous bed.

While a portion of reactant gas may be dissolved or entrained in liquid flowing through the bottom reaction zone 25, the major amount of unreacted gas and vapor byproduct is recovered downstream by passing through the secondary containment wall 18 into a plenum chamber 32 and thus through the catalyst support 28 to the outlet. Treated liquid also may pass through this recovery path.

The rate of liquid application to the primary bed surface may exceed the rate at which liquid can be admitted through the foraminous wall 16, resulting in a cascade of overflowing liquid outside the bed and down the outside solid partition and containing catalytic reaction zone 25 to a liquid accumulator chamber 34. Excess liquid may be removed by a sump pump or eductor 36 for recycle to the reactor top by a pressurized gas stream 38.

The present technique is adaptable to a variety of interphase catalytic reactions, particularly for treatment of heavy oils with hydrogen-containing gas at elevated temperature. Industrial processes employing hydrogen, especially petroleum refining, employ recycled impure gas containing 10 to 50 mole % or more of impurities, usually light hydrocarbons and nitrogen. Such reactant gases are available and useful herein, especially for high temperature hydrogenation or hydrogenolysis at super-atmospheric pressure.

In the refining of lubricants derived from petroleum by fractionation of crude oil, a series of catalytic reactions are employed to severely hydrotreat, convert and remove sulfur and nitrogen contaminants, hydrocracking and isomerizing components of the lubricant charge stock in one or more catalytic reactors. This can be followed by hydrodewaxing and/or hydrogenation (mild hydrotreating) in contact with different catalysts under varying reaction conditions. An integrated three-step lube refining process disclosed by Garwood et al, in U.S. Pat. No. 4,283,271 is adaptable to crosscurrent processing according to the present invention.

At the point of entry the reactant gas has its greatest concentration. Depletion of the gaseous reactant downstream will increase the relative concentration of inerts and/or byproduct vapors. Likewise, the liquid being treated is generally more reactive at the upper end of the reactor system where it contacts the fresh reactant gaseous phase.

In a typical multi-phase reactor system, the average gas-liquid volume ratio in the catalyst zone is about 1:4 to 20:1 under process conditions. Preferably the liquid is supplied to the catalyst bed at a rate to occupy about 10 to 50% of the void volume adjacent the primary bed surface. In those reactions wherein the volume of gas

decreases due to reactant depletion, the volumetric ratio of liquid to gas can increase markedly as the liquid feedstock and gas pass through the reactor. Vapor production, adiabatic heating or expansion can also affect the volume. In general, the quantity of unreacted gas in the contact zone should be adequate to provide a mixed phase bulk density of at least 10% of the bulk density of the liquid phase (at reaction conditions).

Advantageously, the multi-phase reactor system is operated to achieve uniform distribution. If too little liquid flux is maintained, the catalyst surface in the porous bed may become dry or permit excessive channeling of the gas phase. Flow rates for both reactant phases are controlled within constraints, whereby proper operation of the reactor can be assured.

In order to maintain a desirable uniform flow of reactant streams through the fixed catalyst bed, adequate flow paths for liquid and gaseous phases should be provided. In a continuous process the ratio of reactant gas to liquid feedstock and the space velocity of reactants relative to catalyst must be carefully considered. Achievement of uniform liquid flow through a porous bed of solids can be obtained if the catalyst is properly distributed and shaped. The void volume in a reaction zone is a function of catalyst configuration and loading technique. While a densely packed bed of spherical solids may be employed to place a maximum amount of catalyst in a predetermined reactor volume, the low void fraction may interfere with fluid flow, especially where crosscurrent flow of two phases is required. Advantageously, the catalyst bed has a void volume fraction greater than 0.25. Void fractions from 0.3 to 0.9 can be achieved using loosely packed polylobal or cylindrical extrudates. Hollow ring-type supported catalysts, such as Raschig rings or the like, permit liquids to flow downwardly through the porous bed by gravity while the gas phase flows transversely through the denser liquid, providing a horizontal liquid flow component for uniformly wetting catalyst to enhance mass transfer and catalytic phenomena.

Catalyst size can vary widely within the inventive concept, depending upon process conditions and reactor structure. If a low space velocity or long residence in the catalytic reaction zone is permissible, catalysts having an average maximum dimension of 1 to 5 mm may be employed. Relatively small catalyst particles may be loaded randomly to assure uniformity and larger supported catalysts may be averaged in a geometric pattern to achieve optimum bed utilization.

Reactor configuration is an important consideration in the design of a continuously operating system. In its simplest form, a vertical pressure vessel is provided with a catalyst bed of rectangular cross-section. A typical vertical reactor having a catalyst bed length to average width ratio of about 1:1 to 8:1 is preferred. A single bed or a stacked series of beds may be retained within the same reactor shell. Reactors of uniform horizontal cross section may be employed and other non-uniform configurations, such as conoidal reactors, tapered vessels, etc., may also be employed.

An alternative embodiment of the invention is depicted in FIG. 2, which is a vertical cross-section view of the top and middle portions of a reactor vessel with a conoidally shaped catalyst bed. A pressurized shell 110 having a top liquid inlet 112 receives a liquid stream from pump 113. A fixed bed of contact solids 115 is contained by a frustoconical outer screen wall 116 and a conical inner screen wall 118 uniformly spaced from

the outer wall to provide for radial gas flow there-through. The height of the bed above the inner apex is substantially equal to the bed thickness between primary and secondary conoidal surfaces. Catalyst particles may be held in place by a top layer of inert balls 119. The bed may be supported and fluids withdrawn in the manner of FIG. 1. Liquid is distributed separately from the gas via header conduit 120 and spray nozzles 122; however, any suitable means for uniformly introducing liquid through the primary surfaces 116, 119 may be employed. Excess liquid is withdrawn through annular chamber 134. Pressurized gas enters through inlet port 138 and flows evenly to the primary bed surface and thence transversely through the bed 115 in the direction of least pressure drop. The main gas flow is substantially perpendicular to the containment walls 116, 118, with a minor amount entering via the flat top portion 119 into the frustrum shaped bed. It should be understood that the bed may also be supported as an inverted cone on Y-shaped configuration with liquid applied inside and above, and gas flowing radially out.

In order to demonstrate the inventive concept, a typical bed profile is represented in FIGS. 3 and 4. The liquid streamlines (solid) shown in FIG. 3 represent the direction of liquid flow for oil entering a porous bed at spaced points along the outer primary bed surface. Corresponding gas streamlines (dashed) depict the cross flow principle. The profiles in FIGS. 3 and 4 are based on a catalytic hydrodewaxing process employing heavy petroleum gas oil lubricant feedstock at a liquid space velocity of  $1 \text{ hr}^{-1}$  over a randomly packed bed of 1.5 mm extrudate catalyst of the ZSM-5 type having a porosity (apparent void volume fraction) of 0.36. The hydrocarbon oil has a viscosity of 0.4 centipoise. The reactant gas is fed at a uniform rate of 2100 std. ft.<sup>3</sup>/barrel of oil, with a pressure drop of 0.1 psi (690 Pascals) across an 8 foot thickness of the bed. The profile section height is 25 feet and maximum base dimension from center to outer wall is 15 feet.

As shown in FIG. 3, the liquid streamlines are substantially uniform, especially for liquid entering in the top portion of the bed. The vertical gravity flow component is the predominant flow vector, with the horizontal component induced by gas averaging about 5 to 10% of the vertical.

FIG. 4 is a graphic plot of pressure, which depicts incremental pressures from the inlet pressure of about 3500 kPa (500 psi). The isobars show calculated pressure drop at 70 Pascal increments across the bed. The combination of horizontal and vertical motions provide in more complete wetting of the catalyst bed by the oil and hence more efficient use of the catalyst volume. The large exposed area of catalyst surface in the sloping bed also contributes to improved oil distribution.

The advantages of the present invention include: (1) uniform liquid residence time in contact with the catalyst (2) crosscurrent flow pattern, decreasing the need for large volumes of gas and alleviating flow maldistribution characteristic of prior art mixed phase cocurrent flow; (3) transversely flowing gas mixing the downward moving liquid and thus facilitating intimate contact between the gas, liquid, and solid (catalyst) phases.

While the invention has been explained by reference to preferred embodiments, there is no intent to limit the inventive concept, except as set forth in the following claims.

What is claimed is:

1. In the process of treating a liquid hydrocarbon stream with a gaseous reactant stream in a porous bed of solid catalyst particles, an improved technique for maintaining uniform distribution of liquid and gas phases comprising:

containing the porous bed of solid particulates so as to define an upper and lower contact zone wherein said upper contact zone is defined by a primary bed surface sloping outwardly and downwardly from the upper contact zone toward the lower contact zone, and a secondary bed surface parallel to said primary bed surface, said primary bed surface admitting at least a portion of the liquid stream into the porous bed, while permitting the unadmitted portion of the liquid stream to flow by gravity downwardly across said primary bed surface; distributing the liquid stream at spaced points across said primary bed surface; maintaining gravity flow of liquid through said porous bed; introducing the gaseous stream to the contact zone through the primary bed surface and directing the gas flow toward the secondary bed surface transverse to liquid flow; and recovering the treated hydrocarbon liquid and gas streams.

2. In the process of treating a liquid stream with a gaseous stream according to claim 1, wherein said hydrocarbon comprises a waxy oil, said gaseous reactant comprises hydrogen and said catalyst particles comprises a siliceous zeolite having a constraint index of about 1 to 12, for selective hydrodewaxing of the hydrocarbon stream.

3. In the process of treating a liquid stream with a gaseous stream according to claim 2, wherein said zeolite consists essentially of an acidic ZSM-5 type pentasil aluminosilicate having a silica to alumina mole ratio greater than 12.

4. In the process of treating a liquid stream with a gaseous stream in a contact zone containing a porous bed of contact solids, an improved technique for maintaining uniform distribution of liquid and gas phases comprising

containing the porous bed of contact solids to define upper and lower zones wherein said upper contact zone is defined by a primary bed surface sloping outwardly and downwardly from said upper contact zone toward said lower contact zone, said primary bed surface facing the distributed liquid stream to admit at least a portion of the liquid stream into the porous bed through said primary bed surface, while permitting unadmitted liquid to flow by gravity downwardly across the sloping primary surface;

distributing the liquid stream at spaced points across the contact solids at a primary bed surface; maintaining gravity flow of liquid through said porous bed;

containing contact solids with a secondary bed surface substantially parallel to said primary bed surface;

introducing the gaseous stream to the contact zone through the primary bed surface and directing the gas flow toward the secondary bed surface transverse to liquid flow at sufficient rate to drive gravitating liquid with a horizontal vector; and recovering the treated liquid and gas streams downstream from the porous bed.

7

5. The process of claim 4 wherein the contact solids have a porosity void fraction of at least 0.25 and an average liquid void saturation of about 0.15 to 0.50.

6. The process of claim 4 wherein liquid streamlines from the primary bed surface to the secondary bed surface have an average horizontal vector at least 5% of the corresponding vertical vector.

7. A multiphase cross-current catalytic reactor comprising

a reactor vessel having inlet means for liquid and gaseous reactant streams;

catalyst containment means within said reactor vessel for retaining a fixed porous bed of catalyst particles; said containment means comprising a plurality of foraminous side walls for admitting and removing reactant gas in crosscurrent flow transverse to gravitating liquid flow, where said foraminous side walls define an upper contact zone and a lower contact zone, wherein at least one of said foraminous side walls slopes outwardly and away from said upper zone to said lower zone;

8

liquid distributor means adapted for applying liquid reactant onto a top portion of said upper zone;

liquid projection means for distributing a reactant liquid stream onto said outwardly sloping foraminous surface whereby the liquid reactant stream passes through said foraminous side wall into the porous catalyst bed; and

means for recovering catalytically treated liquid from said porous bed.

8. The reactor of claim 7 wherein the catalyst bed has a void volume fraction of about 0.25 to 0.50.

9. The reactor of claim 7 wherein the porous bed has a frustroconical shape.

10. The reactor of claim 7 further comprising gas plenum means for recovering reactant gas from the porous bed.

11. The reactor of claim 10 comprising pump means for supplying liquid reactant to the catalyst bed at a rate sufficient to occupy about 10 to 50 percent of the void volume thereof.

\* \* \* \* \*

25

30

35

40

45

50

55

60

65

**Studies in Surface Science and Catalysis**

Advisory Editors: B. Delmon and J.T. Yates

Vol. 76

# FLUID CATALYTIC CRACKING: SCIENCE AND TECHNOLOGY

Editors

**John S. Magee**

*Catalytic Science Associates, 12205 Mount Albert Road, Ellicott City,  
Maryland 21042, U.S.A. (Formerly Director of Technology, Katalistiks  
International, A Unit of UOP, Baltimore, Maryland, U.S.A.)*

**Maurice M. Mitchell, Jr.**

*Ohio University Southern Campus, 1804 Liberty Avenue, Ironton,  
Ohio 45638, U.S.A. (Formerly Vice President, Research and Development,  
Ashland Petroleum Company, Ashland, Kentucky, U.S.A.)*



ELSEVIER    Amsterdam — London — New York — Tokyo    1993



ELSEVIER SCIENCE PUBLISHERS B.V.  
Sara Burgerhartstraat 25  
P.O. Box 211, 1000 AE Amsterdam, The Netherlands

ISBN: 0-444-89037-8

© 1993 Elsevier Science Publishers B.V. All rights reserved.

No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording or otherwise, without the prior written permission of the publisher, Elsevier Science Publishers B.V., Copyright & Permissions Department, P.O. Box 521, 1000 AM Amsterdam, The Netherlands.

Special regulations for readers in the U.S.A. - This publication has been registered with the Copyright Clearance Center Inc. (CCC), Salem, Massachusetts. Information can be obtained from the CCC about conditions under which photocopies of parts of this publication may be made in the U.S.A. All other copyright questions, including photocopying outside of the U.S.A., should be referred to the publisher.

No responsibility is assumed by the publisher for any injury and/or damage to persons or property as a matter of products liability, negligence or otherwise, or from any use or operation of any methods, products, instructions or ideas contained in the material herein.

This book is printed on acid-free paper.

Printed in The Netherlands

s 35, 217-235 (1987).  
4 (1978).  
r., Applied Catalysis 71

hoolsby, AIChE Spring

l C. R. Johnson, NPRA

atent 4,929,336 (1990).  
AM-91-40 (1991).

3,773 (1983).

fr., S. Takase, and M.

992).

D. Kowalczyk, Warren  
tional Meeting, Paper

Petroleum Chemistry,

Meeting (1991).

## CHAPTER 10

### METALS PASSIVATION

RICHARD H. NIELSEN and PATRICIA K. DOOLIN

Research and Development Department  
Ashland Petroleum Company  
P.O. Box 391  
Ashland, Kentucky 41114

#### 1. INTRODUCTION

An important factor behind the growth of resid cracking discussed in Chapter 9 is the development of heavy metals passivation technology. Compared to gas oils, resids usually contain high concentrations of heavy metals (nickel, vanadium, and iron) primarily in the form of porphyrin complexes and salts of organic acids. Under cracking conditions, metals, notably nickel and vanadium in gas oils as well as resids, deposit on the cracking catalyst and catalyze undesirable dehydrogenation reactions. High sodium levels poison acid sites of the cracking catalyst. Vanadium (and possibly sodium) under the conditions of the FCCU regenerator destroy the zeolitic component of the catalyst. Active metals reduce the yield of gasoline and increase the yields of hydrogen and coke. Since most cracking units can handle only limited amounts of hydrogen and coke, the level of active metals on the catalyst must be controlled in order to achieve maximum throughput and profit. Metals passivation is the process of mitigating the deleterious effects of contaminant metals thereby improving the catalyst activity and/or selectivity to more desired products. In the case of passivation of vanadium, the average life of the cracking catalyst particle is prolonged. With nickel, passivation decreases dehydrogenation activity. The refiner usually has several ways to utilize the benefits of reduced yields of hydrogen and coke achieved through metals passivation. One economically attractive option for many refiners has been to crack resid blended with the traditional gas oil feed.

Since 1976, the successful commercial use of antimony passivation agents has provided refiners with a cost effective process requiring little capital and operating costs to manage mainly nickel. Bismuth and cerium compounds are now also commercially successful. Since 1982 tin and, more recently, rare earth

compounds have been commercially successful in passivating vanadium. A number of other elements are now known to provide some degree of metals passivation.

Other ways to handle heavy metals in the catalytic cracker are catalyst withdrawal and replacement (flushing) with lower metals equilibrium or fresh catalyst, optimizing process conditions to temper the effects of the metals, and using a more metals tolerant cracking catalyst. Catalyst flushing has been commonplace in the United States and Europe creating a market for low metals equilibrium catalyst often used for replacement. However, using high catalyst replacement rates or process conditions is generally limited by economics and effectiveness to relatively low metals levels.

Even when hydrotreating the cracker feedstock, metals passivation is often beneficial, i.e. by reducing the economically optimum degree of hydrotreater severity. Operating the feed hydrotreater to meet sulfur specifications instead of low metals results in slower rate of contaminant metal build up on the HDS catalyst, extending the bed life.

While it is well known that substantial benefits can be gained by passivating high metals containing catalyst, recent experience shows significant benefits may be realized at low nickel loadings, about 500 ppm nickel, or in some instances when hydrogen is produced at only 40-55 SCF/BFF [1,2]. However, each FCC unit requires detailed evaluation to determine the benefits of passivation.

Metals passivation is accomplished today in two ways: 1) metering the metals passivation agent, usually via the fresh feed, into the cracker where it deposits on the catalyst or 2) incorporating additives during manufacture into the catalyst formulation or into a separate carrier particle which is blended with the catalyst. Passivation additives are normally referred to as metal traps.

This chapter reviews the present knowledge of metals passivation of FCC catalysts. Useful information for the refinery engineer, the manager and the researcher is presented. Metals deactivation chemistry and laboratory and commercial passivation experience are discussed, primarily for nickel and vanadium.

## 2. CHEMISTRY OF METALS DEACTIVATION

Both nickel and vanadium function as dehydrogenation catalysts at FCC reactor conditions [3]. The dehydrogenation activity of vanadium is generally thought to be about one-fourth to one-fifth that of nickel [4]. Traditionally the relative dehydrogenation activity of contaminant metals is expressed in the passivation literature as a single parameter for metal concentration: four times the nickel level plus the vanadium concentration ( $4\text{Ni} + \text{V}$ ).

ing vanadium. A num-  
ber of metals passiva-

tic cracker are catalyst  
its equilibrium or fresh  
fects of the metals, and  
flushing has been com-  
market for low metals  
ver using high catalyst  
ited by economics and

metals passivation is  
y optimum degree of  
meet sulfur specifica-  
amnant metal build up

be gained by passivat-  
ows significant benefits  
on nickel, or in some  
VBT [1,2]. However,  
the benefits of passiva-

ways: 1) metering the  
the cracker where it  
ing manufacture into  
which is blended with  
as metal traps.

is passivation of FCC  
the manager and the  
laboratory and com-  
nickel and vanadium.

Non catalysts at FCC  
vanadium is generally  
[4]. Traditionally the  
expressed in the pas-  
ation four times the

Vanadium reacts destructively with the zeolitic component of the cracking catalyst causing loss of crystallinity which is a more critical problem than its dehydrogenation activity. Nickel does not cause structural damage to the zeolitic cracking catalyst, but significantly alters product selectivity to increase coke and gas yields. High hydrogen production reduces gasoline volumetric yield and limits compressor throughput. When determined separately, the relative activity of contaminant metals to degrade catalyst surface area are ranked as  $\text{Ni} < \text{Fe} < \text{Na} \ll \text{V}$  (Figure 1 [5]). Iron is usually associated with the catalyst primarily as a tramp metal. A small quantity is deposited by iron porphyrins which are present in the crude oil. With sodium removed by a properly working desalter, nickel and vanadium are the primary contaminant metals of a typical FCC feedstock.

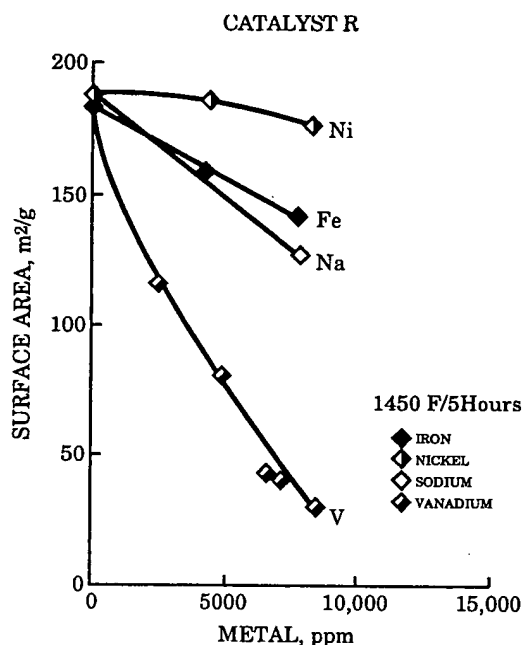


Figure 1. Metals degrade surface area. Reprinted with permission from [5]. Copyright 1983 American Chemical Society.

## 2.1 Nickel

Under FCC reactor conditions, nickel is a dehydrogenation catalyst producing high yields of hydrogen and coke. The extent of dehydrogenation depends upon the nickel content, the age of the nickel and the cracking catalyst type. Although nickel is not considered to be a major factor causing loss of cata-

lyst activity, studies have shown that nickel containing catalysts produce more heavy cycle oil which is indicative of a reduced ability to crack the heavier feed components. As heavy oil conversion is normally associated with the catalyst matrix, this would imply that nickel poisons mild acid sites present on the matrix as well as stronger sites on the zeolite exterior surface. This explanation would be in agreement with the observed location of nickel (external to zeolite) on commercial catalyst using secondary ion mass spectroscopy (SIMS) [6]. Nickel has also been shown to be catalytically active in the regenerator producing high concentrations of carbon dioxide [7]. As the oxidation of carbon to carbon dioxide produces approximately 3.5 times the heat of the oxidation of carbon to carbon monoxide, processing high nickel feed can result in reduced unit throughput.

As with other metals, commercial cracking catalysts vary in their sensitivity to nickel poisoning. Electron spectroscopy for chemical analysis (ESCA) studies show that nickel on equilibrium catalyst exists as  $\text{Ni}^{+2}$  and  $\text{Ni}^{+3}$  [6]. X-ray photoelectron spectroscopy (XPS) studies indicate that Ni interacts with clay and gel components of FCC cracking catalysts to form  $\text{NiAl}_2\text{O}_4$  surface species. In steam-aged catalysts, silica is found to migrate to the surface where, in the presence of Ni, it forms inert  $\text{NiSiO}_3$ -like species. The ability of a catalyst matrix (non-zeolitic component) to minimize nickel dispersion or of a clay to form inert nickel species will determine the Ni tolerance of the catalyst. The most active nickel species are produced when nickel combines with alumina or extraframework material present in modified zeolite [8].

Variation of nickel dehydrogenation activity was observed on different supports. Various laboratory techniques have been utilized to effectively study nickel interactions. Temperature programmed reduction (TPR) studies have been useful to investigate these different nickel species. Nickel on alumina was found to be difficult to reduce. The extent of reduction of nickel on alumina supported catalysts increased with increasing nickel loading [9] and increasing reduction temperature [10]. Bartholomew and Pannell [9] reported 29% reduction for a 0.5% Ni on alumina and 75% reduction for a 9% Ni on alumina catalyst reduced at 450°C. For Ni-silica catalysts the extent of reduction was usually higher than that for alumina-supported systems [9,11], due to a lower interaction with the support. The active nickel species producing hydrogen and coke was found to vary on the cracking catalysts based upon these factors. Nickel was generally more active on catalysts which contained alumina species which could interact with the nickel.

Imaging SIMS has shown that nickel tended to be immobilized once deposited on the catalyst particle [3]. Palmer and Cornelius [12] correlated catalyst age with nickel content using data from equilibrium catalyst which they fractionated by gradient density separation. The amount of nickel deposited was found to be the product of the feed rate and the feed nickel content divided by the inventory over time in the unit. This relationship can be used to determine

talysts produce more  
crack the heavier feed  
ed with the catalyst  
present on the matrix  
his explanation would  
ial to zeolite) on com-  
IMS) [6]. Nickel has  
producing high con-  
on to carbon dioxide  
of carbon to carbon  
unit throughput.

vary in their sensi-  
cal analysis (ESCA)  
+2 and Ni+3 [6]. X-  
at Ni interacts with  
m  $\text{NiAl}_2\text{O}_4$  surface  
o the surface where,  
e ability of a catalyst  
n or of a clay to form  
catalyst. The most  
es with alumina or

observed on different  
to effectively study  
(TPR) studies have  
ckel on alumina was  
ckel on alumina sup-  
[9] and increasing  
reported 29% reduc-  
on alumina catalyst  
duction was usually  
a lower interaction  
rogen and coke was  
factors. Nickel was  
species which could

immobilized once  
[12] correlated cata-  
catalyst which they  
nickel deposited was  
content divided by  
used to determine

the average age of catalyst in the unit by dividing the observed nickel content by its deposition rate. As nickel ages, it losses dehydrogenation activity and the required amount of passivation agent decreases [13].

## 2.2 Vanadium

Some of the largest natural resources of vanadium are certain crudes from Mexico and Venezuela. However, vanadium is present to some extent in virtually all crudes. Vanadium compounds in crude oil are primarily porphyrin complexes or naphthenates. Naphthenates decompose fully below 525-30°C; however, porphyrins decompose only after one-half hour at these conditions [14]. Cracking may or may not be complete in the short contact time of the modern FCC riser. Whether or not complete decomposition occurs through riser cracking or by combustion in the regenerator, it is generally agreed that vanadium is deposited on the exterior of the catalyst particle due to the polar nature and size of the porphyrin molecule. Since the coked catalyst is carried into the regenerator of the fluid catalytic cracker, a portion of vanadium present on the catalyst is oxidized to V+5. ESCA studies of equilibrium and metal-impregnated fresh catalysts show vanadium only in the +5 valence state [15]. Another study indicates that approximately 5% of the vanadium is present as VO+2 species on a steamed Y zeolite [15]. However, it is generally agreed that the primary species of vanadium is +5 after steaming. The vanadium oxidation state is independent of the vanadium source contained in the crude. As the cracking catalyst is repeatedly transported from the regenerator to the reactor and back again, the vanadium continually undergoes valence changes between +5 and +4. Once formed in the regenerator, V+5 does not readily reduce to a +3 valence under normal fluid catalytic cracking reactor conditions [15].

Vanadium deposition on the cracking catalyst results in substantial loss of catalyst surface area and activity. As the zeolite component is the highest surface area component of the modern cracking catalyst, a decline in surface area is primarily associated with loss of zeolite crystallinity. Catalytic activity is effected similarly by contamination by sodium or vanadium (Figure 2 [5]) although caused by zeolite acid site poisoning versus zeolite destruction, respectively. Vanadium has been reported to be less destructive to the zeolite in the presence of nickel [4,11].

Vanadium deposited on the catalyst exterior gradually migrates from the matrix surface to the zeolite crystal where it reacts destructively with the zeolite. The mechanism of this attack is a subject of considerable controversy. Several papers published in the early 1980's propose interaction of vanadium pentoxide ( $\text{V}_2\text{O}_5$ ) with the zeolite to form a low-melting eutectic [14]. Vanadium pentoxide is known to have a low melting point, 690°C, which is lower than the average FCC regenerator temperature of 720°C. Hettinger and coworkers [5] clearly demonstrated that an oxidative atmosphere is necessary for zeolite destruction. Therefore, a V+5 species is usually assumed to be responsible for

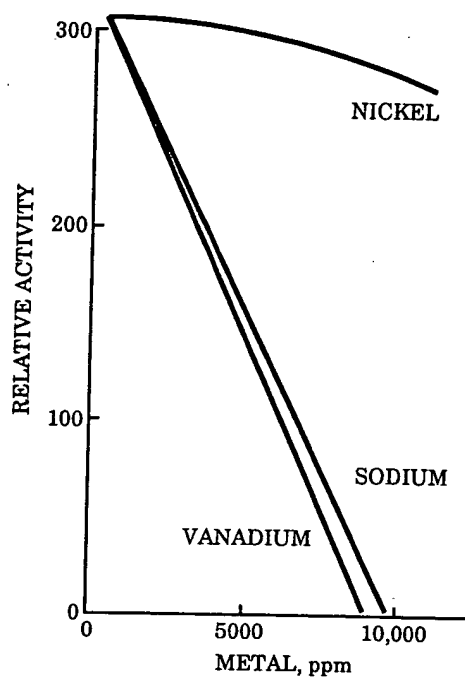


Figure 2. Relative activity loss due to metals. Reprinted with permission from [5]. Copyright 1983 American Chemical Society.

the destruction of zeolite. Most of the damage to the zeolite is expected to occur in the regenerator. Further evidence is that the destructive properties of vanadium can be mitigated by using hydrogen as a reducing agent at high temperatures [5]. These conditions are thought to reduce the V+5 species and, therefore, prevent its effect on the zeolite.

Vanadates of rare earths or aluminum were identified in studies conducted using physical mixtures of catalyst or catalyst components and vanadium pentoxide powder. The mixtures were calcined to high temperatures and characterized. Studies using laser Raman spectroscopy, XPS, and X-ray diffraction (XRD) on equilibrium catalyst showed a variety of phase changes occur with the destruction of zeolite by vanadium. Calcined rare-earth-exchanged Y (CREY) collapsed with the formation of cerium orthovanadate ( $\text{CeVO}_4$ ) whereas HY formed mullite ( $\text{Al}_6\text{Si}_2\text{O}_{13}$ ) and silica (tridymite) [15]. Mullite formation was also observed in steam-aged V-loaded gels but not when nickel was present. These studies led to theories of zeolite destruction by the formation of such compounds with abstracted atoms from the zeolite which lead to structural collapse. For example, Pompe [14] proposed the destruction of REY resulted when  $\text{V}_2\text{O}_5$

attacked the rare earth component of the zeolite forming a low melting point RE-vanadate phase in which RE-ions were incorporated in varying proportions because of their chemical similarity. Although these compounds were formed, these studies did not establish whether their formation caused zeolite destruction or whether they were simply formed subsequent to the zeolite destruction.

These theories were later questioned by researchers who found that  $V_2O_5$  did not cause zeolite structural damage in the absence of steam [16]. If sintering were the operative mechanism, destruction should have taken place in dry air. In the absence of steam, no zeolite destruction occurred. In 1986, Wormsbecher, Peters and Maselli proposed vanadic acid as the vanadium species responsible for zeolite destruction. The acid,  $H_3VO_4$ , would be formed under FCC regenerator conditions by the reaction  $V_2O_5(s) + 3H_2O(v) \rightarrow 2H_3VO_4(v)$  [16]. This hypothesis incorporated both the oxygen and steam requirements. Since vanadic acid is a strong acid analogous to  $H_3PO_4$ , acid attack of the zeolite via hydrolysis of the  $SiO_2/Al_2O_3$  framework seemed plausible. The instability of zeolites to acid attack was well documented. However, this theory did not explain why catalysts which contain high sodium levels were even less vanadium tolerant than those with low levels. Sodium ions would be expected to have a neutralizing effect and to improve vanadium tolerance.

Vanadium was found to be equally destructive whether added to the catalyst by naphthenate impregnation or by physical mixture of  $V_2O_5$  powder. X-ray adsorption spectroscopy (XAS) studies found the vanadium adsorption edges were identical for steamed catalyst exposed to vanadium by impregnation or physical mixture, indicating the same oxidation state and coordination geometry [17]. Electron microprobe studies showed that after steam treatment vanadium was evenly distributed throughout the catalyst particle in each case. Wormsbecher contended that a volatile species must be responsible for a small amount of  $V_2O_5$  powder to cause the same destruction as vanadium impregnation [16]. Liquid wetting or solid-state reaction could not account for deactivation by small amounts of  $V_2O_5$  powder. To prove that zeolite destruction was caused by a volatile species, transport experiments were carried out in a flowing tube reactor. In these experiments, the zeolite containing catalyst was physically separated from a source of  $V_2O_5$  powder. High temperature water was injected above the  $V_2O_5$  in flowing air. Even though the vanadium source and the catalyst did not come into contact, after several hours the zeolite had completely lost crystallinity. Hence, the precursor for vanadium poisoning must involve  $H_2O$  vapor and  $V_2O_5$ ; the resulting species must be volatile. Compounds of vanadium with oxidation states lower than +5 were not considered as they did not exist at FCC regenerator conditions.

Recently Pine [18] studied vanadium destruction using a solid-state kinetics approach. He proposed that pentavalent vanadium simply served as a catalyst for the steam destruction of zeolite. The rate constants for crystallinity loss



were found to be directly proportional to the vanadium concentration. This would be true whether the role of vanadium was that of a reactant or of a catalyst. However, the fact that very small amounts of vanadium have a large effect on the reaction rate without being consumed was more consistent with a catalytic role. Pine extrapolated the rate constants obtained with vanadium to zero concentration and found agreement with rate constants taken without vanadium. This fact was consistent with the conclusion that the reaction was the well-known steam destruction of zeolite. To further understand the location of vanadium attack in the zeolite, rate constants were determined for silicalite, CREY and USY (ultrastable Y) in the presence and absence of vanadium. Silicalite was found to have a low vanadium tolerance. CREY and USY were found to have the same vanadium tolerance even though the CREY had almost 5 times as many framework aluminum atoms per unit cell. Based on these findings, the Si-OH bond was considered the more probable site of attack. This was consistent with the lower steam stability of a small particle Y zeolite which would have a high surface area to volume ratio. In addition, contrary to other studies [19], sodium and vanadium independently were found to have the same catalytic activity for steam destruction of zeolite, and together they acted synergistically. From the kinetic results Pine concluded both materials enhance the rate of reaction of steam with the zeolite. However, Pine did not explain the mechanism of this synergetic effect.

At the time of this writing, a known mechanism of vanadium attack which explains all observed phenomena is not available. Although current knowledge is inadequate from an academic perspective, the factors which lead to vanadium deactivation of cracking catalysts such as oxidation state of the vanadium, and the presence of steam and high temperature are clearly defined.

### 3. FCC PASSIVATION ADDITIVES

Numerous strategies to deal with the deleterious effects of metals, primarily nickel and vanadium, have been developed. These include hydrotreatment to remove metals from the resid FCC feed [20], operational changes to alter the oxidation states of metals [5], and passivation agents (for list of suppliers see [21]). The use of metal passivation has become an established practice. A passivation agent is a compound which can be utilized in an FCC unit under normal operating conditions. Passivation additives can also include metals traps or scavengers which are mixed with the catalyst or compounds which are incorporated in the catalyst during manufacture.

### 4. NICKEL PASSIVATION AGENTS

Nickel passivation agents are normally injected into the FCC feedstock to react with the contaminated catalyst. Although a large number of elements are